Chiral cyclopalladium (II) complexes promoted asymmetric synthesis of optically active functionalized bidentate phosphine ligands

Tang, Lulu

2008

Tang, L. L. (2008). Chiral cyclopalladium(II) complexes promoted asymmetric synthesis of optically active functionalized bidentate phosphine ligands. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/13620>

<https://doi.org/10.32657/10356/13620>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**CHIRAL CYCLOPALLADIUM(II) COMPLEXES
PROMOTED ASYMMETRIC SYNTHESIS OF
OPTICALLY ACTIVE FUNCTIONALIZED
BIDENTATE PHOSPHINE LIGANDS**

CHIRAL CYCLOPALLADIUM(II) COMPLEXES PROMOTED ASYMMETRIC SYNTHESIS OF
OPTICALLY ACTIVE FUNCTIONALIZED BIDENTATE PHOSPHINE LIGANDS

TANG LULU

TANG LULU

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2008

2008

CHIRAL CYCLOPALLADIUM(II) COMPLEXES PROMOTED ASYMMETRIC SYNTHESIS OF OPTICALLY ACTIVE FUNCTIONALIZED BIDENTATE PHOSPHINE LIGANDS

TANG LULU

School of Physical and Mathematical Sciences

A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
Doctor of Philosophy

2008

ACKNOWLEDGEMENT

I owe a debt of gratitude to many people at Nanyang Technological University for their support and encouragement throughout the years I worked on this thesis. First of all, I am greatly thankful to my supervisor, Prof. Leung Pak Hing, for his instruction and guidance during my whole research work. He for many years encouraged me with his understanding in the value of this project and supported me with his excellent suggestions for improvement and with his strong academic knowledge through chiral phosphine chemistry. Without his enthusiasm and encouragement, this work could not have been done.

Ms. Han Yanhui from NMR Spectroscopy Laboratory offered valuable advice on how to operate various NMR experiment and how to interpret 1D and 2D spectra. Dr. Kok Lip Lin, Ms. Tan Geok Kheng, Prof. Mok Kum-Fun and Dr. Li Yongxin from X-ray Crystallography Laboratory offered excellent expertise and advice on X-ray crystallography, and solved the crystal structures, which is very important to the characterization of chiral complexes. I am very grateful to them. Thanks also go to the staff members of the Mass Spectrometry Laboratory and the Elemental Analysis Laboratories for their contribution and assistance. I am particularly thankful to my senior laboratory mates and good friends, Dr. Yeo Wee Chuan, Dr. Joseph Ng Kok Peng and Ms. Chen Shuli for offering their inspiring suggestions and sharing their thoughts, and to Dr. Pullakat Sumod A. and Dr. Ben Tan Kien Wee for their kindly help being available at all times. I would also like to thank Mr. Zhang Yi for his contribution and continuing my project discussed in Chapter 5. I owe Nanyang Technology University a special word of thanks for generously providing Ph.D scholarship and such a great research environment to me.

To my parents and my husband, I owe thanks beyond measure. They have given me their unquestioning support and thorough understanding throughout these years. Their encouragement has been a constant source of motivation.

TABLE OF CONTENTS

1	Introduction.....	1
1-1	Classification and Preparation of Chiral Cyclopalladated Complexes	1
1-1.1	Cyclopalladated Complexes with Stereogenic Centres Directly Linked to the Metal Centres (Classes A and B Complexes)	2
1-1.2	Cyclopalladated Complexes Containing Stereogenic Centres away from Palladium(II) Centre	5
1-1.2.1	Asymmetric Synthesis	5
1-1.2.2	Resolution	8
1-1.3	Planar Chiral Palladacycles.....	9
1-2	Chiral Cyclopalladated Complexes as Resolution Reagent.....	13
1-3	Chiral Cyclopalladated Complexes Promoting Asymmetric Synthesis.....	19
1-3.1	Catalysts for Allylic Imidates Rearrangement	20
1-3.1.1	[3,3]-Sigmatropic Rearrangement of Allylic Imidates to Allylic Amides	20
1-3.1.2	Catalysts Containing Oxazoline and Diamine Ligands	21
1-3.1.3	Neutral Catalysts	22
1-3.2	Catalysts for C-C or C-Heteroatom Bond Forming Reactions	24
1-3.2.1	Asymmetric Aldol Reaction.....	24
1-3.2.2	Asymmetric Michael Reaction	26
1-3.2.3	Asymmetric Heck Reaction	27
1-3.2.4	Asymmetric Crossing-Coupling Reaction	27
1-3.2.5	Asymmetric Allylic Alkylation Reaction.....	28
1-3.3	Stoichiometric Insertion Reaction.....	29
1-3.4	Stoichiometric Diels-Alder Reactions	32

1-3.4.1	Asymmetric Synthesis of Monophosphines by <i>endo</i> -Cycloaddition Reaction	32
1-3.4.2	Enhanced Stereoselectivity by Using Improved Chiral Palladium(II) Template	34
1-3.4.3	Asymmetric Synthesis of Monophosphines by <i>exo</i> -Cycloaddition Reaction	35
1-3.4.4	Asymmetric Synthesis of Bidentate Phosphine or Arsine Ligands	37
1-3.4.5	Asymmetric Synthesis of Chiral Ligands Containing P(V) Species	39
1-3.5	Stoichiometric Hydroamination and Hydrophosphination Reaction	41
1-4	Objectives of the Present Project	42
2	Chemoselective and Asymmetric Oxidation of a Prochiral Triphosphine to Form a Chiral Diphosphine Ligand	44
2-1	Introduction	44
2-2	Results and Discussion	45
2-2.1	Synthesis of an Equilibrium Mixture of Four Diastereomeric Complexes 134a, b and 135a, b	45
2-2.2	Oxidation of Complexes 134 and 135 with H ₂ O ₂ and Liberation of Enantiomerically Pure Phosphine Mono-Oxide Ligand	52
2-2.3	Oxidation of Complexes 134 and 135 with S ₈ and Liberation of Enantiomerically Pure Phosphine Mono-Sulfide Ligand	58
2-2.4	Oxidation of Complexes 134 and 135 with Se	63
2-3	Conclusion	64
2-4	Experimental Section	64
3	Chemoselective and Stereoselective Oxidation of Triphosphine Ligand Containing a P-stereogenic Centre	70
3-1	Introduction	70

3-2	Results and Discussion	71
3-2.1	Isolation and Characterization of Complex (S,S,Sp)-152a.....	71
3-2.2	Liberation of Ligand (R,Rp)-158 and Establishment of Complexes 152 and 154	78
3-2.3	Attempts to Synthesize P-N Hetero Ligand.....	80
3-3	Conclusion	83
3-4	Experimental Section	83
4	Chiral Palladium Template Induced Asymmetric Synthesis of Bidentate P-Chiral Phosphines Ligands Containing P(V) Groups	87
4-1	Introduction.....	87
4-2	Results and Discussion	88
4-2.1	Fluxional Structure.....	88
4-2.2	Selective Conversion of P(III) to P(V)	91
4-2.3	Asymmetric Alkylation Reaction.....	102
4-2.4	Removal of Chiral Auxiliary from (S,Sp)-165a, (S,Sp)-167a, (S,Sp)-169a to Generate (Sp)-173, (Sp)-174 and (Sp)-175	106
4-2.5	Liberation of Free Ligand (Sp)-176	113
4-2.6	Removal of Palladium Centre from Complexes (Sp)-174 and (Sp)-175	116
4-3	Conclusion	117
4-4	Experimental Section	118
5	Chiral Palladium Template Induced Asymmetric Hydrophosphination Reaction	123
5-1	Introduction.....	123
5-2	Results and Discussion	125
5-2.1	Hydrophosphination Reaction between Diphenyl(styryl)phosphine and Diphenylphosphine	125
5-2.2	Hydrophosphination Reaction of Diphenylphosphine and DMAD.....	131

5-3	Conclusion	136
5-4	Experimental Section	137
	Conclusion	139
	References	142
	Publications.....	153
	Appendix.....	154

SUMMARY

In this thesis, a systematic review of chiral cyclopalladated complexes is described in Chapter 1. This chapter reviews the classification of chiral palladium(II) complexes, and synthetic method of chiral palladium(II) complexes. In addition, their major applications in catalytic asymmetric synthesis including C-C bond formation reaction and C-Heteroatom bond formation reaction, together with their application in asymmetric stoichiometric reactions including asymmetric insertion reaction, Diels-Alder reaction, and hydroamination reaction are discussed.

In Chapter 2, the selective oxidation of a *C*-prochiral tridentate phosphine ligand with hydrogen peroxide, elemental sulfur or elemental selenium in the presence of an optically active palladium(II) template are thoroughly investigated. Two synthetic methods are tried out to obtain an equilibrium mixture of up to four diastereomeric precursors. The insertion of P(O)-H moiety in P(O)Ph₂H into the activated C-C double bond in 1,1-bis(diphenylphosphino)ethene was conducted in order to verify the presence of a four-membered ring intermediate in the corresponding equilibrium mixture. The liberated enantiomerically pure triphosphine mono-oxide and triphosphine mono-sulfide ligands were re-coordinated to a homochiral palladium(II) template. Thus four diastereomeric phosphine-palladium(II) complexes generated after selective oxidation reaction were identified.

In Chapter 3, resolution of a racemic triphosphine ligand containing a *C*-prochiral and *P*-stereogenic centres by metal complexation followed by selective oxidation performed by hydrogen peroxide is demonstrated. Theoretically, up to eight diastereomeric products could be produced, as three stereogenic centres appeared in each diastereomeric complex together with the relative arrangement of the four asymmetric donors at palladium(II) centre. Only five of them were predominately obtained, and the major isomer could be isolated into its optically pure form in a high yield. Accordingly the liberated

enantiomerically pure triphosphine mono-oxide ligands containing both *C*- and *P*-stereogenic centres in one molecule was re-coordinated to *S*- or *R*-form chiral palladium(II) template. Thus four diastereomeric phosphine-palladium(II) complexes generated in the mixture of five diastereomeric products after selective oxidation reaction were identified. Apart from secondary phosphine ligands, a N-H moiety in benzyl amine was attempted to be added into the activated double bond in 1,1-bis(diphenylphosphino)ethylene. A P-N hetero five-membered ring was formed at the palladium(II) centre, however the isolated product was confirmed to be a racemic dichloro palladium(II) complex, so was the liberated P-N hetero ligand.

In Chapter 4, selective oxidation of a *P*-prochiral tridentate phosphine ligand bis(2-diphenylphosphinoethyl)phenylphosphine by using hydrogen peroxide, elemental sulfur or elemental selenium to generate a *P*-chiral tridentate phosphine ligand is thoroughly investigated. The major phosphine-palladium(II) diastereomeric product in each selective oxidation was able to be isolated into its enantiomerically active form. Only the chiral ligand with mono-oxide functional group was stable after removal from palladium(II) stabilization. The rest two chiral ligands containing mono-sulfide and mono-selenide functional groups were found racemized after removal from palladium(II) stabilization. Therefore only the four diastereomeric phosphine-palladium(II) complexes generated after selective oxidation reaction performed by hydrogen peroxide were identified.

In Chapter 5, addition of diphenylphosphine to *cis*- or *trans*-diphenyl(styryl)phosphine in the presence of a chiral palladium(II) template is demonstrated. Attempts to isolate either phosphine-palladium(II) product in its enantiomerically active form were unsuccessful. The separated neutral dichloro palladium(II) complex was found to be a racemic one, so was the liberated ligand. Besides, addition of diphenylphosphine into an activated triple bond in dimethyl acetylene

dicarboxylate in the presence of a chiral palladium(II) template was also demonstrated in Chapter 5. Two diastereomeric products were formed, although theoretically up to four diastereomers could be generated as three stereogenic centres appeared in each diastereomeric complex. Attempts to isolate either of them in its enantiomerically active form were unsuccessful. Therefore acid treatment was performed in order to remove the chiral auxiliary at the palladium(II) template. A mixture of isomeric neutral dichloro palladium(II) complexes enriched in one optical form was obtained. The enriched isomer could be separated into its enantiomerically pure form and the corresponding chiral diphosphine ligand having C_2 symmetry was liberated from palladium(II) stabilization. Accordingly the two diastereomeric phosphine-palladium(II) complexes generated after hydrophosphination reaction were identified.

ABBREVIATIONS AND SYMBOLS

Ac	acetate
Ar	aryl group
<i>ax</i>	axial
Bu	butyl
<i>ca.</i>	about (Latin <i>circa</i>)
calcd	calculated
CDA	chiral derivatizing agent
COD	cyclooctadiene
conc.	concentrated
COSY	correlation spectroscopy
d	doublet
dd	doublet of a doublet
ddd	doublet of a doublet of a doublet
dba	dibenzylideneacetone
decomp.	Decomposed
DMPP	3, 4-dimethyl-1-diphenylphosphole
DMSO	Dimethyl sulfoxide
dppe	1, 2 – bis(diphenylphosphino)ethane
dq	doublet of a quartet
equiv.	equivalent
Et	ethyl
<i>et al.</i>	and others (Latin <i>et alii</i>)
g	gram(s)
Hz	hertz

<i>i</i>	iso
<i>o</i>	ortho
<i>m</i>	meta
<i>p</i>	para
<i>t</i>	tert
LDA	lithium diisopropylamide
m	multiplet
Me	methyl
mg	milligram(s)
mp.	melting point
NMR	Nuclear Magnetic Resonance
NOE	Nuclear Overhauser Effect
Ph	phenyl
Pr	propyl
ppm	parts per million
q	quartet
<i>R</i>	<i>rectus</i> (Latin: right absolute configuration)
ROESY	2D rotating frame nuclear overhauser enhancement
<i>S</i>	<i>sinister</i> (latin: left absolute configuration)
s	singlet
t	triplet
THF	tetrahydrofuran
Å	angstrom(s)
δ	NMR spectroscopy chemical shift in ppm
$[\alpha]_D$	specific optical rotation measures at D line (589nm)

LIST OF ISOLATED NEW LIGANDS AND COMPLEXES

(S,S)-144a

(S,S,Sp)-152a

X=O (S,Sp)-165a

X=S (S,Sp)-167a

X=Se (S,Sp)-169a

(S,Sp)-171a

(S,Rp)-172a

138

(S)-141

(S)-146

(S,Sp)-157

161

(Sp)-174

(Sp)-175

181

(R,R)-184

(R)-142

(R)-147

(R,Rp)-159

(S)-176

(R,R)-185

LIST OF FIGURES

Figure 2.1 Crystal Structure of Dichloro Complex 138.....	50
Figure 2.2 Crystal Structure of Complex (S)-141	55
Figure 2.3 Crystal Structure of Complex (S,S)-144a	61
Figure 3.1 Crystal Structure of Complex (S,S,Sp)-152a	76
Figure 3.2 Crystal Structure of Complex 161	82
Figure 4.1 VT ^{31}P $\{^1\text{H}\}$ NMR Spectrum of Complex 164 in CDCl_3	90
Figure 4.2 VT ^{31}P $\{^1\text{H}\}$ NMR Spectrum of Complex 164 in DMSO-d_6	91
Figure 4.3 Crystal Structure of Complex (S,Sp)-165a.....	94
Figure 4.4 Crystal Structure of Complex (S,Sp)-167a.....	97
Figure 4.5 Crystal Structure of Complex (S,Sp)-169a.....	100
Figure 4.6 Crystal Structure of Complex (S,Sp)-171a	104
Figure 4.7 Crystal Structure of Complex (S,Rp)-172a.....	105
Figure 4.8 VT ^{31}P $\{^1\text{H}\}$ NMR Spectrum of Complex (Sp)-174 in CDCl_3	108
Figure 4.9 Crystal Structure of Complex (Sp)-174	109
Figure 4.10 Crystal Structure of Complex (Sp)-175	112
Figure 5.1 Crystal Structure of Complex (S,S)-181a	127
Figure 5.2 Crystal Structure of Complex (S,R)-181b.....	128
Figure 5.3 Crystal Structure of Dichloro Complex (R,R)-184.....	134

LIST OF TABLES

Table 2.1 Selected Bond Lengths (Å) and Angles (deg) for Dichloro Complex 138	51
Table 2.2 Selected Bond Lengths (Å) and Angles (deg) for Dichloro Complex (S)-141 ..	56
Table 2.3 Selected Bond Lengths (Å) and Angles (deg) for Complex (S,S)-144a.....	60
Table 3.1 Selected Bond Lengths (Å) and Angles (deg) for Complex (S,S,Sp)-152a.....	77
Table 3.2 Selected Bond Lengths (Å) and Angles (deg) for Dichloro Complex 161	83
Table 4.1 Selected Bond Lengths (Å) and Angles (deg) for Complex (S,Sp)-165a.....	95
Table 4.2 Selected Bond Lengths (Å) and Angles (deg) for Complex (S,Sp)-167a.....	98
Table 4.3 Selected Bond Lengths (Å) and Angles (deg) for Complex (S,Sp)-169a.....	101
Table 4.4 Selected Bond Lengths (Å) and Angles (deg) for Complexes (S,Sp)-171a and (S,Rp)-172a	106
Table 4.5 Selected Bond Lengths (Å) and Angles (deg) for Complex (Sp)-174	110
Table 4.6 Selected Bond Lengths (Å) and Angles (deg) for Complex (Sp)-175	113
Table 5.1 Selected Bond Lengths (Å) and Angles (deg) for Complexes 181	129
Table 5.2 Selected Bond Lengths (Å) and Angles (deg) for Dichloro Complex (R,R)-184	135

CHAPTER

1

INTRODUCTION

Chiral phosphines have been receiving great attention, because of their use as ligands in metal catalysts for asymmetric reactions. However, since they are usually air sensitive, the handling and storage of such compounds require an inert atmosphere. Therefore chiral phosphines are normally prepared via the protected form such as their phosphine oxides, phosphine sulfides, phosphonium salts, phosphine-borane adducts and phosphine-metal complexes. Among them, synthesis of optically active phosphines by using chiral cyclopalladium complexes as template and reaction promoter has attracted significant interest. In particular, the applications of chiral palladium(II) cyclometalated-amine complexes are highly successful. As chiral cyclopalladium complexes play the major roles in preparing chiral phosphines, an introduction of these complexes is given as below.

1-1 Classification and Preparation of Chiral Cyclopalladated Complexes

Basically, there are four classes of chiral cyclopalladated compounds, as presented in Fig. 1.1, in terms of different types of chirality¹. In class **A** the stereogenic carbon centre adopts tetrahedral geometry and uses a σ bond directly bonded to the metal centre. While in class **B** the stereogenic centre, which is also directly connecting to the metal centre, is an

asymmetrically substituted donor group such as an amine, phosphine or thioether. Unlike the above two classes, class **C** represents a group of chiral cyclopalladated compounds in which chiral centres are away from the palladium(II) centre; and this type of complexes is perhaps the most thoroughly investigated and widely applied. Planar chirality is exhibited in class **D**, which often contains a ferrocenyl or η^6 -chromium carbonyl moiety. This kind of complexes is becoming more important due to their applications as catalysts in organic synthesis chemistry in the modern world.

Fig. 1.1

1-1.1 Cyclopalladated Complexes with Stereogenic Centres Directly Linked to the Metal Centres (Classes A and B Complexes)

Dating back to the 1970s, complex **1**, one of the first optically active organometallic compounds, was prepared through reaction between 8-ethylquinoline and lithium tetrachloropalladate (Scheme 1.1)². The chlorine-bridge in the organopalladium dimer could be cleaved upon treatment with (1-phenylethyl)amine to give complex **2**, which could be subsequently converted to complex **3**, as the amine ligand was replaced by triphenylphosphine. Being the analogue of complex **1**, the bromine-bridged dimer **5** was prepared via the reaction of organometallic mercury derivative **4** with zerovalent complex of palladium (Scheme 1.2)^{3a}. The overall process was described as insertion of the L₂[Pd(0)] moiety into the mercury-carbon bond followed by elimination of the mercury^{3b}. Similarly the bromine-bridged dimer could be cleaved off by a phosphorus donor ligand. However, only complex (*S,S*)-**7** (Scheme 1.3)⁴ has been characterized by X-ray crystallography, while other chiral complexes (**2-6**) were not crystallographically characterized.

Scheme 1.1

Scheme 1.2

Scheme 1.3

In the meantime, transmetalation reaction with lithiated tertiary amines was also attempted for the purpose of preparing chiral cyclopalladium complexes in Class **A**. Complexes **9**, **10** and **11**⁵ were synthesized via transmetalation reaction (Scheme 1.4)⁶. Only diastereomers (S,S) -**11** and (S,R) -**11** could be separated efficiently. The absolute configuration of (S,S) -**11** was confirmed to be *S* at the Si substituted carbon atom in solid state.

Scheme 1.4

With the development of modern stereochemistry, a large amount of cyclopalladium complexes with hetero chiral centres directly connecting to metal centres were proved to be feasible, such as the phosphapalladacycle (Sp)-**12** (Scheme 1.5)⁷ and the PCP chiral pincer complex **15** (Scheme 1.6)⁸. Additionally, a group of orthopalladated dimers **17** containing stereogenic sulfur atom directly linked to palladium(II) acetate were prepared via the reaction of optically active (1-alkylsufanylethyl)-benzenes **16** and palladium acetate as metalation reagent (Scheme 1.7)⁹.

Scheme 1.5

Scheme 1.6

Scheme 1.7

1-1.2 Cyclopalladated Complexes Containing Stereogenic Centres away from Palladium(II) Centre

Common enantiopure palladacycles of class **C** (Fig. 1.1) are typically formed by orthometalation reaction. There are two general approaches to prepare these chiral cyclopalladium complexes in their enantiomerically pure forms: reacting of palladium reagent and enantiomerically pure amines directly or reacting of palladium reagent with racemic amines followed by isolation of two diastereomeric products into their enantiomerically pure forms.

1-1.2.1 Asymmetric Synthesis

Usually asymmetric synthesis route requires enantiomerically pure ligands. The most commonly used ones are organic amines. As presented in Scheme 1.8-1.13, most of these optically active amines reacted smoothly with palladium reagent. In some cases, basic conditions are required in order to remove a carbon-proton to form a Pd-C bond.

Scheme 1.8

Scheme 1.9

Scheme 1.10

Scheme 1.11

Scheme 1.12

Scheme 1.13

Complexes **18** and **19**¹⁰ were initially prepared through orthometalation reaction between $\text{Na}_2[\text{PdCl}_4]$ and optically active amines $\text{PhCH}(\text{Me})\text{NMe}_2$ (Scheme 1.8) or *N,N*-dimethyl- α -(2-naphthyl)ethylamine (Scheme 1.9), respectively, together with the presence of triethylamine as a proton acceptor. An improved procedure was published two years later¹¹: $\text{Na}_2[\text{PdCl}_4]$ was replaced by $\text{Li}_2[\text{PdCl}_4]$ which was generated in situ from LiCl and PdCl_2 to produce complex **18**. Similarly the synthesis of complex **19** was found more efficient by using $\text{Li}_2[\text{PdCl}_4]$ instead of $\text{Na}_2[\text{PdCl}_4]$ ¹². Their naphthylamine analogue complex **20** (Scheme 1.10)¹³ and phenanthrene analogue complex **24** (Scheme 1.14)¹⁴ were later reported to be synthesized by using a similar approach. Other sterically demanding complexes **21**¹⁵, **22-23**¹⁶, **25**¹⁷, **26**¹⁸ were prepared via orthopalladation reaction with various metalation reagent and the appropriate optically active amines (Scheme 1.11-1.13 and 1.15-1.16).

Scheme 1.14

Scheme 1.15

Scheme 1.16

1-1.2.2 Resolution

The resolution approach involves synthesis of a mixture of racemic cyclopalladium complexes, followed by reacting with appropriate chiral reagent to produce a pair of diastereomeric complexes. Subsequently the mixture of diastereomeric complexes can be separated by fractional crystallization and the desired chiral cyclopalladium complexes can be liberated from the separated diastereomerically pure complexes, respectively. For example, the racemic complex **27** can be resolved into their optically pure form (*R*)-**27** and (*S*)-**27** (Scheme 1.17)¹⁹, by using sodium proline as the resolving reagent, respectively. It is interesting to note that in both of the two resolved isomers, the methyl group (*Me*₁) at the phenyl ring adjacent to the chiral carbon atom locked the methyl substituent (*Me*₃) at the chiral carbon atom axially only, either in solid state or solution. Besides, the methyl group (*Me*₂) at the phenyl ring adjacent to the palladium(II) centre functions as an efficient chiral directing group¹⁹. The advantages of complex **27** make it used as a good reaction promoter for asymmetric Diels-Alder reaction, which will be discussed in Scheme 1.63. Interestingly, complexes **28a** with a P donor ligand and **28b** with an As donor ligand (Scheme 1.18) were resolved by using a chiral cyclopalladium complex (*R*)-**20** as a resolving reagent²⁰.

Scheme 1.17

Scheme 1.18

1-1.3 Planar Chiral Palladacycles

Planar chiral palladacycles are usually obtained by direct C-H activation route. Generally, there are three independent methods¹ for asymmetric C-H activation such as by using a chiral base for enantioselective deprotonation, introducing a chiral directing group, or applying an asymmetric ligand for exchange. The resulting complexes can be separated via crystallization or chromatography.

Cyclopalladated derivatives of ferrocene compose the majority of planar chiral palladacycles. Among them anion-bridged planar chiral dimers exhibit more complex structures and interesting aspects of stereo-isomerism. Theoretically, there are six possible diastereomeric di- μ -chloro-bridged dimers of a planar chiral cyclopalladated ferrocenyline (Fig. 1.2)²¹, classified mainly by the arrangement of the pair of coordinating nitrogen atoms either adopting a *trans* position [*syn*-(*Rp,Rp*), *syn*-(*Sp,Sp*) and *anti*-(*Rp,Sp*)] or a *cis* position [*syn*-(*Rp,Sp*), *anti*-(*Sp, Sp*) and *anti*-(*Rp,Rp*)].

Fig. 1.2

Complexes **29a** [*syn*-(*Rp,Rp*)], **29b** [*syn*-(*Sp,Sp*)], and **29c** [*syn*-(*Rp,Sp*)] were generated in a reaction (Scheme 1.19)^{21, 22} and were separated by chromatography. The absolute configurations as well as that of **30** obtained as *anti*-(*Rp,Rp*) type (Scheme 1.20)²³ were determined by X-ray crystallography. Another two chiral planar cyclopalladated complexes *anti*-(*Sp,Sp*)-**31**²⁴ (Scheme 1.21) and *anti*-(*Rp,Rp*)-**32**²⁵ (Scheme 1.22) were synthesized via reactions between Na₂PdCl₄ and the corresponding enantiomerically pure ferrocenyl ligands. Additionally dimers (*Sp,Sp*)-**33** and (*Rp,Rp*)-**33** were resolved by L-leucine (Scheme 1.23)²⁶ and complex (*Sp,Sp*)-**35** containing phosphorus donor atom could be resolved by (*S*)-proline (Scheme 1.24)²⁷.

Scheme 1.19

Scheme 1.20

Scheme 1.21

Scheme 1.22

Scheme 1.23

Scheme 1.24

Some preparation involving ferrocenyl ligands showed high dependency on the condition of reaction. For example the yield of complex **36** was influenced by molar ratio of Pd : ligand. With the molar ratio changed from 1:2 to 1:1, the yield of desired product **36** could be increased (Scheme 1.25)²⁸. Otherwise, if the pH value of reaction mixture was 9.8, complex **37** could be achieved with the best enantioselectivity (Scheme 1.26)²⁹.

Scheme 1.25

Scheme 1.26

1-2 Chiral Cyclopalladated Complexes as Resolution Reagent

In 1970s, the chiral cyclopalladium complex **18** was firstly used for the partial kinetic resolution³⁰. A range of tertiary phosphines of $(\pm)\text{-PR}_1\text{R}_2\text{R}_3$ type have been resolved by complex **18**^{31, 32}. Thereafter the resolution method is well established and it is widely applied to the synthesis of chiral phosphine ligands including simple non-cyclic tertiary phosphines and biaryl ligands of the type P-P, P-N, P-S, etc^{31, 38}. A typical procedure comprises by treating racemic ligands with a chiral cyclopalladated reagent followed by separation of diastereomers using crystallization or chromatography. The corresponding enantiomerically enriched ligands can be subsequently liberated from the palladium(II) centre by the displacement with a chelating ligand (dppe) or a strong donor ligand (cyanide).

Initially kinetic resolution of non-cyclic tertiary phosphines involved 1 mol of palladium(II) dimer reacting with 4 mol of racemic phosphine (Scheme 1.27 and 1.28) followed by isolation of complexes **38** or **40**^{10, 30}, respectively. Treatment of complexes **38** and **40** with $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dppe) would liberate optically active phosphine with optical rotation opposite to that of the phosphine ligand remaining in the original solution.

Degradative hydrogenation of complexes **39** and **41** with NaBH₄ could liberate the starting amine ligand from palladium(II) centre in good yield with retaining optical purity. Therefore the recovered amine could be used for regenerating resolving reagent **18** (Scheme 1.10 and 1.11). Compared with the low efficiency obtained by using of complex **18**, the binuclear enantiomerically pure palladium(II) complex **19** is a much better resolving reagent, especially for aryldialkylphosphines [eg. PPh(*t*-Bu)Me³³ and PPh(*t*-Bu)(*i*-Pr), etc.] (Scheme 1.28)¹⁰.

Scheme 1.27

Scheme 1.28

On the other hand, reaction in Scheme 1.29 involves 1 mol of palladium(II) dimer reacting with 2 mol of racemic arsine³⁴ giving a mixture of two diastereomers. After repeated recrystallization of the initial mixture of diastereoisomers, complex (*S*,*R*_{As})-**42** was isolated in its optically pure form. The attempt of resolution of halophosphine of the type (±)-PXR₁R₂ was not successful³⁵ and little progress has been made in this field³⁶. Although (±)-PClPh(*i*-Pr) (Scheme 1.30) was reported to be resolved by complex (*R*)-**20** by forming a pair of diastereomeric products, yet the corresponding chlorophosphine could not be liberated from complexes **43**. However, the P-Cl group could be converted to the corresponding methoxyphosphine complexes **44** with high stereoselectivity³⁷.

Scheme 1.29

Scheme 1.30

Optically active chelating di(tertiary phosphine) are good auxiliaries for the asymmetric hydrogenation of prochiral substrate molecules. Therefore a large number of such ligands are attempted to be prepared, mainly by resolution. It should be noted that chelating ligands containing tertiary phosphines or arsines are generally easier to be resolved than the mono-dentate counterparts³¹, due to their strong coordination properties. Accordingly the economic resolving reagent complex **18** is usually used for this purpose. The common procedure normally requires an anion exchange process with NH_4PF_6 (Scheme 1.31-1.34)³⁸ after a bridge-splitting reaction. Moreover simple displacement with chelating ligand such as dppe could not displace diphosphine ligand efficiently, as most of the chelating di(tertiary phosphine) are stronger ligands than dppe. The liberation of the optically active chelating di(tertiary phosphine) is performed in two steps: removal of chiral amine auxiliary by treatment with conc. hydrochloric acid giving a dichloro neutral palladium(II) complex, and ligand displacement with cyanide subsequent.

Scheme 1.31

Scheme 1.32

Scheme 1.33

Scheme 1.34

It has been well established that the coordination of unsymmetrical bidentates to complexes **18** or **20** is remarkably regiospecific with the softer donor invariably occupying the position *trans* to the *NMe*₂ group of the chiral auxiliary³¹. Thus chiral chelating bidentate ligands including P-As (Scheme 1.35-1.37)³⁹ will coordinate to palladium(II) centre with phosphorus atom specifically occupied the *trans* position to nitrogen atom^{39, 40}. When it comes to P-N (Scheme 1.38-1.40)^{13, 41, 42} and P-O (Scheme 1.41, 1.42)⁴³ ligands, the more efficient resolving reagent **20** was mostly utilized.

Scheme 1.35

Scheme 1.36

Scheme 1.37

Scheme 1.38

Scheme 1.39

Scheme 1.40

Scheme 1.41

1-3 Chiral Cyclopalladated Complexes Promoting Asymmetric Synthesis

Chiral cyclopalladated complexes are useful in asymmetric synthesis both as catalysts and as stoichiometric templates. Being used as catalysts, enantiomeric cyclopalladated complexes are well studied in allylic rearrangements and C-C bond forming reactions; meanwhile being used as stoichiometric templates, Diels-Alder reaction, insertion reactions, hydroamination and hydrophosphination reactions have been investigated intensively.

1-3.1 Catalysts for Allylic Imidates Rearrangement

1-3.1.1 [3,3]-Sigmatropic Rearrangement of Allylic Imidates to Allylic Amides

The [3,3]-sigmatropic rearrangements have been investigated for a few decades and widely used in organic chemistry synthesis. Among them (Scheme 1.42), Cope (**62**, X=Y=C) and Claisen (**62**, X=O, Y=C) rearrangements are more classic. The rearrangement of allylic imidates (**62**, X=O, Y=N) to allylic amides (**64**, X=O, Y=N) is significantly important since it converts the readily available allylic alcohols to other less available allylic amines⁴⁴⁻⁴⁶. With the first rearrangement of allylic trichloroacetimidates to allylic trichloroacetamides (**65** to **66**, Scheme 1.43) introduced in 1976⁴⁷, the synthesis of nitrogen containing materials such as alkaloids, antibiotics, unnatural amino acids and drug candidates becomes an important research topic⁴⁸.

Scheme 1.42

Scheme 1.43

The transformation of allylic trichloroacetimidates to allylic trichloroacetamides (Scheme 1.43) can be achieved with metal catalysts⁴⁴ containing Ni(0), Pd(0), Ag(I), Ni(II), Pd(II), Pt(II), Hg(II) and Al(III) centres. Usually [3,3]-sigmatropic rearrangements catalyzed by Hg(II) and Pd(II)^{45, 49} take place through a cyclization induced rearrangement (CIR) mechanism⁵⁰, which involves coordination of the metal catalyst (M, Scheme 1.42) to the alkene **62** to form the cyclic intermediate **63** followed by bond breaking in either of two following possible pathways: rupture of bond **a** to go back to starting material **62** or break of bond **b** to generate product **64**.

1-3.1.2 Catalysts Containing Oxazoline and Diamine Ligands

The first generation⁵¹ of palladium(II) catalysts for rearrangement of allylic imidates contains coordinated planar nitrogen atoms such as complexes **67-70** (Fig. 1.3). Although the cationic oxazoline catalysts for the rearrangement of imidate **71** to **72** (Scheme 1.44) gave only 30% ee^{51b}, this achievement proved the possibility to obtain nonracemic allylic amide with an asymmetric palladium(II) catalyst and inspired the improvement on the designing of catalysts. The poor stereoselectivity in this early asymmetric catalysis is attributed to the fact that palladium(II) diamine catalysts produced cationic complexes during the catalysis process, which did not match the CIR mechanism model (Scheme 1.43)⁵².

Fig. 1.3

Scheme 1.44

1-3.1.3 Neutral Catalysts

Asymmetric cyclopalladated catalysts containing ferrocenyl moiety, chromium tricarbonyl moiety and (η^4 -tetraphenylcyclobutadiene) cobalt moiety, which would generate neutral activated complexes during catalysis process, were synthesized and investigated.

Complex **73** (Fig. 1.4) is one of the first cyclopalladated ferrocenyl chloro bridged dimers used as catalysts for allylic imide rearrangement⁵². It was evaluated for the rearrangement of allylic imide **77** to allylic amide **78** (Scheme 1.45) and the enantiomeric excess was found to be 67%. Catalysts **76**⁵³, as well as complexes **73-75** (Fig. 1.4), are among the first few catalysts with projecting steric influence both above and below the square plane of a chiral palladium(II) complex. Unlike the chloro-bridged dimer, the iodide-bridged dimers **79** (Fig. 1.5) needed to be deiodinated to become active catalysts⁵⁸. The use of **80-82** (Fig. 1.5), which were prepared by iodination insertion of palladium(II) to the ferrocenecarboxylic acid and enantiopure amino alcohols, as catalysts could easily achieve 90% ee^{54, 55}.

Fig. 1.4

Scheme 1.45

Fig. 1.5

Other than the ferrocenyl moiety, chiral cyclopalladium complexes containing chromium tricarbonyl can also function as catalysts of [3,3]-sigmatropic rearrangement⁵⁶. For example, the in situ generated catalyst by deiodination of chromium tricarbonyl complex **83**, **84** (Fig. 1.6) catalyzed the rearrangement of allylic imide **77** to give allylic amide **78** (Scheme 1.45) in 75% yield and 80% ee.

Fig. 1.6

Apart from ferrocenyl moiety, (η^4 -tetraphenylcyclobutadiene) cobalt was also involved in this type of catalysts⁵⁷⁻⁵⁹. In certain cases, catalysts **85** and **86** (Fig. 1.7) show more superiority as they are soluble in a variety of dried solvents and can be stored at room temperature for several months without diminishing their catalytic activity^{57b}.

Fig. 1.7

1-3.2 Catalysts for C-C or C-Heteroatom Bond Forming Reactions

Palladium(II) catalysts provide an abundance of possibilities of C-C and C-heteroatom bond formation, which is important in organic synthesis. To date, palladacycles are amongst the most active catalysts in Heck type C-C and related C-heteroatom bond forming reactions⁶⁰. Typically chiral pincer PCP palladium(II) complexes have been treated as Lewis acids and testified to be good catalysts for asymmetric Aldol- and Michael-type reactions, coupling reactions and allylic alkylation.

1-3.2.1 Asymmetric Aldol Reaction

The aldol reaction is one of the fundamental organic transformations because it involves the formation of a C-C bond and the creation of two chiral centres simultaneously. In order to enhance stereoselectivity, chiral auxiliaries are incorporated into either of the two reacting components or both of them. The asymmetric aldol condensation reaction was initially catalyzed by a gold catalyst⁶¹ and further studied by using palladium(II) catalysts⁶².

This class of reaction has been proved to be performed well in enantioselectivity by using PCP-Pd catalysts⁶³. Complex **87**⁶³ functions as a catalyst precursor for the asymmetric aldol reaction between methyl isocyanoacetate and aldehydes (Scheme 1.46)⁶⁵. The discovery on the effects of solvents showed that in THF the reaction gave higher

enantioselectivity (24% *trans*-**88**, 67% *cis*-**88**); while the investigation of a variety of organic bases showed little influence on the enantioselectivity.

With a palladium(II) complex **89**⁶⁴ having P*CP* ligand as the catalyst, a higher yield (94-98%) was obtained for *trans* product (complexes **90a** and **90b**) of the aldol condensation reaction (Scheme 1.47)⁶⁶, however the enantiomeric excess was never found to be higher than 11%.

Scheme 1.46

Scheme 1.47

1-3.2.2 Asymmetric Michael Reaction

Michael addition of cyanocarboxylates is usually catalyzed by chiral phosphine-rhodium complexes giving high enantioselectivity, and only scattered attention has been paid to the use of palladium(II) catalysts⁶⁷.

Chiral palladium(II) complexes **91**⁶⁸ with C_2 -symmetric ligands have been used as catalysts for the Michael reaction between cyanoacetate and methyl vinyl ketone (Scheme 1.48). For this reaction, the best result obtained was 95% yield and 28% ee⁶⁹.

In contrast to the normal metal-introduction route, ligand introduction route was applied to the synthesis of complex **92** (Scheme 1.49). This was caused by the corresponding pincer ligands showed little reactivity to palladium due to the steric bulkiness of the pyrroloimidazolone groups⁶⁷. Complex **92** was investigated as catalyst for the asymmetric Michael reaction of vinyl ketones and α -cyanocarboxylates as nucleophiles. The best result was achieved as 89% yield and 81% ee⁷⁰.

Scheme 1.48

Scheme 1.49

Scheme 1.50

1-3.2.3 Asymmetric Heck Reaction

The Heck reaction, described as addition of vinyl or substituted vinyl groups to organic halides or triflates⁷¹, is usually catalysed by palladium(0) compounds. Thus the use of a chiral palladium(II) complex is less well documented. When it comes to asymmetric catalysis, many palladium(II) complexes incorporating cyclometallated phosphines^{71c,71d}, chelating diphosphine ligands are found efficient. Moreover the tridentate PCP pincer palladium(II) complexes **89** are also found to be excellent catalysts^{71b}. On the other hand, in some cases, poor enantiomeric excesses (close to zero in most cases)⁷² were resulted. The lack of selectivity in these processes is mainly due to the real catalytic species are nanoparticles of palladium(0) generated by decomposition of the catalyst^{71e}. After losing of the chiral environment, chiral palladium(II) catalysts showed little superiority in asymmetric Heck reaction.

1-3.2.4 Asymmetric Crossing-Coupling Reaction

Crossing-Coupling reactions are well presented by synthesizing of optically active biaryls having 1, 1'-binaphthyls, which are widely used as auxiliaries for a variety of synthetic asymmetric reactions⁷³. Complex **93**^{73c} was found to be the best catalyst for cross-coupling reactions in both catalytic activity and enantioselectivity. The enantiomeric purity of monoalkylated biaryls (**94a** and **94b**) could reach as high as 93% ee⁷⁴.

Scheme 1.51

1-3.2.5 Asymmetric Allylic Alkylation Reaction

Allylic alkylations catalyzed by chiral palladium(II) complexes have achieved excellent enantioselectivities by using optically active bidentate phosphine and phosphine-nitrogen ligands as catalysts⁷⁵. Chiral bidentate ligand **96**⁷⁶ differs only from tridentate ligand **95**⁷⁶ by substituting the pyridine ring with benzene ring^{75c, d}. The allylic alkylation reaction of racemic 1,3-diphenyl-2-propenyl acetate and dimethyl malonate (Scheme 1.52)⁷⁷ generated optically active product up to 75% ee and 97% yield by using catalyst containing ligand **95**; 60% ee and 93% yield by using catalyst containing ligand **96**.

Scheme 1.52

1-3.3 Stoichiometric Insertion Reaction

During the stoichiometric processes, the stereochemical integrity of the starting palladacycle can be passed onto the product. Substituted alkynes and alkenes can readily insert into Pd-C bonds⁷⁸ with either retention or inversion of stereochemistry. The Pd-C bond in cyclopalladated complexes containing N-donor ligands (such as complexes **18**, **19** etc.) shows variable reactivity toward alkyne insertion⁷⁹. In addition, the effects that come from the electron donor/acceptor nature of the alkyne substituents, the structure of the palladacycle and the nature of the other ligands coordinated to palladium(II) could not be ignored.

As illustrated in Scheme 1.53-1.55⁸⁰, electron-deficient alkynes could insert into Pd-C bonds of the palladacycles **97** giving adducts **98**, which meant that even the coordinated bulky groups present, the insertion reaction will not be inhibited. Interestingly, the coordinated DMPP ligands in complexes **97** could function as diene and reacts with alkynes to achieve [4+2] Diels-Alder cycloadditions (Scheme 1.61 and 1.62)⁸¹.

Scheme 1.53

Scheme 1.54

Scheme 1.55

Chiral palladium(II) complexes with planar chirality could also be involved in stoichiometric insertion reaction. The first bi-insertion products of planar chiral cyclopalladated ferrocenes with alkynes were demonstrated in Scheme 1.56, 1.57. Chiral palladium(II) complexes **99** reacting with diphenylacetylene yielded the corresponding bisalkyne insertion complexes **100**^{82a}.

Scheme 1.56

Scheme 1.57

If complex **29a** reacted with stoichiometric amounts of diphenylacetylene, mono-insertion of alkyne would occur to produce complex **101a**; on the other hand when complex **29a** reacted with excess diphenylacetylene, bi-insertion occurred and complex **101b** was generated (Scheme 1.58). That, a variety of anion-bridged (chloro, nitrito, thiocyanato and acetato) planar chiral dimeric cyclopalladated derivatives of ferrocene reacted with diphenylacetylene to generate bis(alkyne) insertion products, has also been reported (Scheme 1.59)^{82b}.

Scheme 1.58

Scheme 1.59

1-3.4 Stoichiometric Diels-Alder Reactions

Diels-Alder reaction is a valuable reaction because high regio- and stereo-selectivity can be obtained together with the formation of new C-C bonds. The asymmetric Diels-Alder reaction is the most efficient method for the construction of chiral six-membered rings. Most asymmetric Diels-Alder reactions depend on the use of a chiral diene or a dienophile containing a chiral auxiliary group. Recently palladium(II) complexes containing chiral amine auxiliaries are used successfully in promoting [4+2] cycloaddition for asymmetric synthesis of functionalized phosphine ligands⁸³. The five-membered heterocycle 3,4-dimethyl-1-phenylphosphole (DMPP) is a poor diene due to its aromaticity. However, it can be activated upon coordinating to palladium(II) centre and undergoes cycloaddition reactions towards a variety of dienophiles. DMPP or other ligands having soft donors would take up the coordination position *trans* to the NMe_2 group in complexes of the type **18-23** specifically by splitting a Pd-Cl bond. The other coordination position, which is *trans* to the aromatic ring, would be occupied by either chloro ligand or perchlorato group to control the cycloaddition reaction occurring either via *endo*- or *exo*-pathway.

1-3.4.1 Asymmetric Synthesis of Monophosphines by *endo*-Cycloaddition Reaction

The Pd-Cl bonds in complexes **97a**, **97b** and **104** are thermodynamically stable and kinetically inert, which cannot be cleaved by weak donors such as organic dienophiles. Thus the reacting dienophile cannot be involved in any form of metal cocomplexation. Consequently the activated DMPP ligand in the chloro complexes can undergo intermolecular *endo*-cycloaddition reactions. Such an intermolecular process generally yields a pair of diastereomers in *ca* 1:1 ratio as the stereoselectivity could only be controlled by the chiral palladium(II) template via a single P-Pd bond.

Reactions of coordinated DMPP as diene with a variety of poor dienophiles were summarized in Scheme 1.60⁸⁴⁻⁸⁹. Most of the reactions gave a pair of diastereomers in

almost equal quantity with the best selectivity as 1:3 in ratio^{86, 87}. Both complexes **97a** (Scheme 1.61) and **97b** (Scheme 1.62) could react with *N*-phenylmaleimide and undergo diastereoselective [4+2] Diels-Alder cycloaddition giving diastereomers **106a** and **106b**, respectively⁸⁰.

Scheme 1.60

Scheme 1.61

Scheme 1.62

1-3.4.2 Enhanced Stereoselectivity by Using Improved Chiral Palladium(II) Template

It has been reported that for complexes **27** (Scheme 1.17)²⁰ and **24** (Scheme 1.14)¹⁴, the organometallic ring conformation is locked by a spacer and hence the methyl group at the chiral carbon centre adopts axial position in both of complexes **27** and **24**. For their DMPP derivatives, the protrudent methyl group in complex **107** and the bulky substituent in complex **109** acts as stereochemistry controller for their neighboring coordination sites. Significantly higher stereoselectivities were indeed achieved by these templates. For example, by using complex **107**, a mixture of the two expected diastereomers in 1:3.5 ratio was generated with (*S,Rp*)-**108** being the major product (Scheme 1.63)²⁰. When complex **109** was used, the ratio of the two expected diastereomers increased to 1:6 with (*S,Rp*)-**110** being the major product (Scheme 1.64)¹⁴.

Scheme 1.63

Scheme 1.64

1-3.4.3 Asymmetric Synthesis of Monophosphines by *exo*-Cycloaddition Reaction

Removal of the chloro ligand in complex **104** with AgClO_4 , yielded the perchlorato complex **111** in which the Pd-O bond is weak and labile, so that it can be readily displaced by reacting dienophile to form a cationic intermediate. The cycloaddition between the coordinated DMPP and the dienophile thus takes place intramolecularly in an *exo*-pathway.

Scheme 1.65

Scheme 1.66

Scheme 1.67

Some interesting comparisons were reported in the *endo*- and *exo*-cycloaddition reactions promoted by chiral palladium(II) templates⁸³. The *endo*-cycloaddition reactions usually proceeded faster than the corresponding *exo*-cycloaddition reactions, while *exo*-cycloaddition reactions usually produced better stereoselectivities than the corresponding *endo*-cycloaddition reactions. As shown in Scheme 1.65-1.68 *exo*-cycloadduct **112-115**^{84-90, 92} are all the sole products of the reactions between complex **111** and the corresponding dienophiles. Moreover, the cycloaddition reaction between 2-methylene-3-quinuclidone and complex **111** might produce 4 diastereomers as a pair each of stereochemically distinct diastereomeric P-N and P-O cycloadducts; however only the P-N chelating ligand (*R*,*Sp*,*S*)-**116** was formed (Scheme 1.69)⁹³. On the contrary, a 1:1 mixture of the diastereomeric complexes (*R*,*Sp*,*Ss*)-**117** and (*R*,*Sp*,*Rs*)-**117** were formed via the reaction between complex **111** and divinyl sulfoxide (Scheme 1.70)⁹¹.

Scheme 1.68

Scheme 1.69

1-3.4.4 Asymmetric Synthesis of Bidentate Phosphine or Arsine Ligands

Asymmetric Diels-Alder reaction provides an attractive approach of preparing optically active bidentate phosphine ligands enantioselectively by using the chiral palladium(II) complex **20**. Theoretically the stereochemistry of phosphorus atoms and the relative arrangement of the two nonequivalent donor atoms (P or As) will result in more diastereomers in one reaction. However in most cases, only one cycloadduct is generated stereoselectively.

As typical examples (Scheme 1.71, 1.72)⁹⁴, complexes **(R,Sp,S)-118** and **(R,Sp,S)-119** are the sole product when diphenylphosphine and diphenylvinylarsine reacted with coordinated DMPP, respectively^{94c}. The racemic form of methylphenylvinylphosphine split the chloro bridges in **(R)-20** regiospecifically and produced a pair of diastereoisomers (Scheme 1.73)^{95a}. Upon removal of the chloro ligand with treatment of AgClO_4 , the pair of diastereoisomers reacted directly with DMPP and generated two unseparable diastereoisomers **(R,Rp,Sp)-120** and **(R,Sp,Sp)-120**. Interestingly if the derivative complex of **(R)-20** (Scheme 1.10), **(R)-111** reacted with 2 equiv. mol of racemic methylphenylvinylphosphine (Scheme 1.74), **(R,Rp,Sp)-120** was the only cycloaddition product leaving **(R)-methylphenylvinylphosphine** simultaneously⁹⁶. Similarly complexes **(S,Rp,Rp)-121** (Scheme 1.75)⁹⁶, **(S,Rp)-122** (Scheme 1.76)⁹⁷ were generated as the sole products in the corresponding reactions and complex **123** (Scheme 1.77)⁹⁸ was the major product of the reaction between diphenylvinylphosphine and 2-diphenylphosphinofuran.

Scheme 1.71

Scheme 1.72

Scheme 1.73

Scheme 1.74

Scheme 1.75

Scheme 1.76

Scheme 1.77

1-3.4.5 Asymmetric Synthesis of Chiral Ligands Containing P(V) Species

DMPPS (3, 4-dimethyl-1-phenylphosphole 1-sulfide) reacted with diphenylvinylphosphine and produced a pair of diastereomers **(R,Rp)-125** and **(R,Sp)-125** (Scheme 1.78) in the presence of a chiral organopalladium template via an intramolecular mechanism⁹⁹. Upon removal of the naphthylamine auxiliary, a pair of enantiomers enriched in **(Rp)-126** was generated and the major product could be isolated as its enantiomerically pure form successfully. When DMPPS was treated with thiobenzophenone promoted by complex **(S)-60**, a mixture of 1:1 expected cycloadducts **127** (Scheme 1.79) containing S-S

bidentate chelate on the palladium(II) template was generated¹⁰⁵. The asymmetric [4+2] *exo*-cycloaddition reaction between complex (*R*)-**111** and vinyl diphenylphosphine oxide generated (*R,S*)-**128** and (*R,R*)-**128** (Scheme 1.80) in the ratio of 13:1¹⁰⁰.

Scheme 1.78

Scheme 1.79

Scheme 1.80

1-3.5 Stoichiometric Hydroamination and Hydrophosphination Reaction

Palladium-catalyzed hydroamination¹⁰¹ and hydrophosphination reactions are relatively rare. As a breakthrough, di(phenylethynyl)phenylphosphine was reactive toward hydroamination reaction with aniline in the presence of a chiral organopalladium template to give a 4:1 mixture of the chelating diastereomeric *P*-chiral iminophosphine on the chiral template (Scheme 1.81)¹⁰². In addition, the chiral auxiliary promoted the asymmetric hydrophosphination reaction between diphenylphosphine and (*E*)-diphenyl-1-propenylphosphine to give (*R*)-prophos predominantly; while the chiral auxiliary promoted the asymmetric hydrophosphination reaction between diphenylphosphine and (*Z*)-diphenyl-1-propenylphosphine to give (*S*)-prophos predominantly (Scheme 1.82)¹⁰³.

Scheme 1.81

Scheme 1.82

1-4 Objectives of the Present Project

As reviewed earlier, complex **20** and its more soluble derivatives **60** are powerful resolving reagents and reaction promoters especially for asymmetric Diels-Alder reactions. However, the resulting enantiomerically active ligands are mainly limited to mono- or bidentate ligands with limited functional groups. The objective of this project work is to further investigate its application on hydrophosphination reaction and selective oxidation reaction in order to synthesize a wider range of functional bidentate phosphine ligands.

In chapters 2-4, a series of tridentate phosphine ligands will be coordinated to the chiral palladium(II) complex to form a mixture of diastereomeric palladium(II) complexes. It is expected that these tridentate phosphine ligands will function as a bidentate chelate to form a five-membered rings with the palladium(II) centre, leaving one of these phosphine groups dangling freely in each diastereomeric product. In theory the uncoordinated phosphine in each isomeric complex is unprotected and can be oxidized or undergo other chemical transformations. The corresponding functional bidentate phosphine ligands will be liberated according to the established method.

Chapter 2

Chapter 3

Chapter 4

In chapter 5, hydrophosphination of vinylic and alkynyl functional groups in the presence of a chiral palladium(II) template will be reported. The resulting functionalized bidentate phosphine ligands will be liberated according to the established method.

Chapter 5

CHAPTER

2

CHEMOSELECTIVE AND ASYMMETRIC OXIDATION OF A PROCHIRAL TRIPHOSPHINE TO FORM A CHIRAL DIPHOSPHINE LIGAND

2-1 Introduction

1,1-Bis(diphenylphosphino)ethene has been proven to be chemically reactive due to the unsaturated carbon-carbon double bond. It is capable of chelating a wide range of metal substrates¹⁰⁴. It is also a versatile starting material for the synthesis of polyphosphines¹⁰⁵, such as polydentate ligands. To date, design and synthesis of simple polyphosphine ligands are no longer a major challenge for researchers. Much attention has been paid on the optically active di(tertiary phosphines) which have been highly successfully used as chiral auxiliaries in enantioselective catalysis¹⁰⁶. Accordingly, several synthetic routes have been well developed and refined for the synthesis of these ligands, especially via the separation by fractional crystallization of a pair of internally diastereomeric palladium(II) complexes containing the racemic ligand and an optically active orthometallated amine³¹. Based on this method, a series of optically active di(tertiary phosphines) containing stereogenic centres have been successfully isolated⁸³.

In addition to diphosphines, mixed phosphine-phosphine oxide ligands have been proven to be useful in metal catalysis and medicinal research¹⁰⁷. The presence of both soft (phosphorus) and hard (oxygen) donors in one molecule enables the coordination to different types of metal. An important feature of mixed phosphine-phosphine oxide ligands

is their ability to act as hemilabile ligands, which plays an important role in catalytic reactions. Generally such ligands are prepared by selective oxidation of polyphosphines, or via synthesis involving separate phosphorus units joining together to form the mixed phosphine-phosphine oxide ligands. Although selective mono-oxidation of chiral diphosphines has been reported¹⁰⁸, the synthesis of chiral mixed phosphine-phosphine oxide ligands via asymmetric oxidation of polyphosphines has not been developed.

Similar to phosphine oxides, phosphine sulfides are thermally stable^{109a} although the P=S bond is much weaker than P=O bond. There are vast valuable methods for the synthesis of phosphine sulfides including addition of halogen to form the species $R_1R_2R_3PX_2$ and followed by displacement of halogen with hydrogen sulfide. Besides, with treatment of boron trisulfide, chiral tertiary phosphine oxides can be transformed into the corresponding phosphine sulfides with high stereospecificity and retention of configuration^{109c}. Apparently the reaction of S_8 with tertiary phosphines^{109b} is the most direct synthetic approach and generally such a kind of synthesis proceeds smoothly.

In this chapter, chiral bidentate phosphine ligands functionalized by a phosphine mono-oxide or a phosphine mono-sulfide group will be prepared via the hydrophosphination reaction of 1,1-bis(diphenylphosphino)ethene and diphenylphosphine followed by selective oxidation reaction with the presence of a chiral palladium(II) template.

2-2 Results and Discussion

2-2.1 Synthesis of an Equilibrium Mixture of Four Diastereomeric Complexes 134a, b and 135a, b

1,1,2-Tris(diphenylphosphino)ethane was prepared according to the reported procedure¹¹⁰. Upon coordination of 1,1,2-tris(diphenylphosphino)ethane to the chiral

cyclopalladated-amine complex (*S*)-**60**, a mixture of four distinct diastereomers was generated (Scheme 2.1). The ^{31}P $\{^1\text{H}\}$ NMR spectrum of the mixture in CDCl_3 exhibited three sets of three doublet of a doublet resonance signals at δ [-14.7 (dd, $^2J_{\text{PP}} = 19.1$ Hz, $^3J_{\text{PP}} = 22.9$ Hz), 47.5 (dd, $J_{\text{PP}} = 30.5$ Hz, $^2J_{\text{PP}} = 19.1$ Hz) and 55.9 (dd, $J_{\text{PP}} = 30.5$ Hz, $^3J_{\text{PP}} = 22.9$ Hz)], [-13.5 (dd, $^2J_{\text{PP}} = 30.5$ Hz, $^3J_{\text{PP}} = 11.4$ Hz), 33.7 (dd, $J_{\text{PP}} = 34.3$ Hz, $^3J_{\text{PP}} = 11.4$ Hz) and 65.4 (dd, $J_{\text{PP}} = 34.3$ Hz, $^2J_{\text{PP}} = 30.5$ Hz)] and [-16.9 (dd, $^2J_{\text{PP}} = 72.5$ Hz, $^3J_{\text{PP}} = 7.6$ Hz), 39.0 (dd, $J_{\text{PP}} = 26.7$ Hz, $^3J_{\text{PP}} = 7.6$ Hz), and 73.2 (dd, $J_{\text{PP}} = 26.7$ Hz, $^2J_{\text{PP}} = 72.5$ Hz)], which were assigned to complexes **134a**, **134b**, **135b**, respectively. In addition a set of two doublet of a doublet and one triplet resonance signals at δ [-14.3 (t, $^2J_{\text{PP}} = ^3J_{\text{PP}} = 22.9$ Hz), 48.5 (dd, $J_{\text{PP}} = 30.5$ Hz, $^2J_{\text{PP}} = 22.9$ Hz), 55.5 (dd, $J_{\text{PP}} = 30.5$ Hz, $^3J_{\text{PP}} = 22.9$ Hz)] were assigned to complex **135a**. The NMR assignments were based on the comparison of complexes **134** and **135** with their corresponding oxide (**139** and **140**) and sulfide (**144** and **145**) complexes, which will be discussed later. As monitored by the ^{31}P $\{^1\text{H}\}$ NMR spectroscopy, complexes **134** and **135** could isomerize in solution and reach equilibrium in one day giving a final ratio of 17:5:3:2 for isomers **134a** : **153b** : **135a** : **135b**, respectively.

Scheme 2.1

Theoretically the tridentate ligand could chelate to the palladium(II) centre giving complexes with either four- or five-membered rings. Furthermore, it is also capable of forming mono- or bi-dentate complexes. These different modes of coordination would

complicate the resulting mixture. Fortunately, the reaction proceeded selectively as only four diastereomers have been generated: all with five-membered chelating rings (Scheme 2.1). It is noteworthy that two of the phosphorus units of each triphosphine ligand were coordinated to the metal, while the remaining phosphorus unit was in the uncoordinated form. The upfield resonances in the negative region (*ca.* δ -13.5 to *ca.* -16.9) are supportive of the uncoordinated free phosphorus units in the four diastereomers. The downfield resonances of the two coordinated phosphorus units in each complex with large coordination chemical shifts, together with small phosphorus-phosphorus coupling constant between the two coordinated phosphorus units are supportive of the formation of five-membered chelating ring in each complex⁸³. It is noteworthy that the products **134a** and **134b** are regioisomers in which they have the same *S* configuration at the newly formed stereogenic carbon centres, but differ in the relative regio arrangement of the four nonequivalent donor atoms on the palladium(II) centre. Similarly complexes **135a** and **135b** are regioisomers with *R* configuration at the newly generated stereogenic carbon centres.

It has been well established that upon coordination of 1,1-bis(diphenylphosphino)ethene to transition metals, the double bond is particularly activated towards nucleophilic addition with a wide range of nucleophiles such as amines, phosphines¹⁰⁶. Hence an alternative pathway for the synthesis of complexes **134** and **135** is possible via the palladium(II) template promoted nucleophilic addition reaction (Scheme 2.2). The ³¹P {¹H} NMR spectrum of the bidentate chelating palladium(II) complex **136** in CDCl₃ exhibited two doublet of a doublet resonance signals at δ -5.0 and 12.7 with phosphorus-phosphorus coupling constant 25.2 Hz. It is proposed that the nucleophilic addition of diphenylphosphine to the chiral metal template activated 1,1-bis(diphenylphosphino)ethene would produce an intermediate complex **137** initially. It

would then prefer to undergo facile rearrangement in solution to the less strained five-membered ring complexes **134** and **135** subsequently. The transformation was monitored by the ^{31}P $\{^1\text{H}\}$ NMR spectroscopy. Within 2 hours, complexes **134** and **135** were generated predominately and only several weak resonance signals were observed around δ 20, which were presumably due to the various diastereomeric intermediates. Further isomerization among complexes **134** and **135** was observed until equilibrium was obtained after one day at room temperature. The final ratio among them was the same as the one obtained from the first pathway described previously.

Scheme 2.2

In order to verify that the four-membered intermediate complex has been indeed generated during the hydrophosphination reaction between 1,1-bis(diphenylphosphino)ethene and diphenylphosphine (Scheme 2.2), the insertion of P(O)-H moiety in $\text{P(O)Ph}_2\text{H}$ to the activated C-C double bond in 1,1-bis(diphenylphosphino)ethene was tried out. As the coordination chemistry is the primary concern rather than the stereoselectivity in this study, a non-chiral economical palladium(II) complex was used as the reaction promoter. The reaction proceeded smoothly in the presence of acetonitrile coordinated dichloro palladium(II) complex and gave the desired product **138** in quantitative yield (Scheme 2.3). Interestingly, despite the fact that an insoluble complex PdCl_2 was used in this process, the desired product $[\text{Cl}_2\text{Pd(P-P)}]$ **138**

could be generated but with a lower isolated yield. Through the studies of ^{31}P $\{^1\text{H}\}$ NMR spectrum, the two coordinated phosphorus units were chemically and magnetically equivalent and showed one doublet resonance signal at δ -32.5, which was coupled by the phosphine oxide ($^3J_{\text{PP}} = 12.3$ Hz). Similarly the phosphine oxide showed one triplet resonance signal at δ 29.4, which was coupled by the two coordinated phosphorous units. The isolated product was established by X-ray crystallography as two independent molecules in one unit cell (Figure 2.1). Selected bond lengths and angles are listed in Table 2.1. As shown in the molecular structure, the four-membered ring is formed and the diphosphine oxide substituent group is retained as expected in one molecule unit. The geometry at palladium(II) is slightly distorted square plane with small distortion angle (6.5° and 8.2°), and small mean deviation from planarity (0.092 Å and 0.044 Å).

Scheme 2.3

Figure 2.1 Crystal Structure of Dichloro Complex **138**

Table 2.1 Selected Bond Lengths (Å) and Angles (deg) for Dichloro Complex **138**

Pd(1)-P(1)	2.231(1)	Pd(1)-P(2)	2.231(1)
Pd(1)-Cl(1)	2.357(1)	Pd(1)-Cl(2)	2.364(1)
Pd(2)-P(4)	2.221(1)	Pd(2)-P(5)	2.240(1)
Pd(2)-Cl(3)	2.347(1)	Pd(2)-Cl(4)	2.347(1)
O(1)-P(3)	1.483(3)	O(2)-P(6)	1.490(3)
P(1)-C(13)	1.870(3)	P(2)-C(13)	1.853(3)
P(4)-C(51)	1.865(4)	P(5)-C(51)	1.865(4)
P(3)-C(14)	1.819(3)	P(6)-C(52)	1.826(4)
C(13)-C(14)	1.533(4)	C(51)-C(52)	1.508(5)
P(1)-Pd(1)-P(2)	74.0(1)	P(1)-Pd(1)-Cl(1)	94.9(1)
P(2)-Pd(1)-Cl(1)	168.7(1)	P(1)-Pd(1)-Cl(2)	168.9(1)
P(2)-Pd(1)-Cl(2)	96.8(1)	Cl(1)-Pd(1)-Cl(2)	94.2(1)
P(4)-Pd(2)-P(5)	74.6(1)	P(4)-Pd(2)-Cl(3)	95.9(1)
P(5)-Pd(2)-Cl(3)	167.6(1)	P(4)-Pd(2)-Cl(4)	170.0(1)
P(5)-Pd(2)-Cl(4)	95.7(1)	Cl(3)-Pd(2)-Cl(4)	94.2(1)
C(13)-P(1)-Pd(1)	94.5(1)	C(13)-P(2)-Pd(1)	95.0(1)
C(51)-P(4)-Pd(2)	94.8(1)	C(51)-P(5)-Pd(2)	94.2(1)
P(2)-C(13)-P(1)	92.3(1)	P(5)-C(51)-P(4)	92.8(2)

2-2.2 Oxidation of Complexes **134** and **135** with H₂O₂ and Liberation of Enantiomerically Pure Phosphine Mono-Oxide Ligand

Due to the presence of the uncoordinated phosphines, the equilibrium mixture of **134** and **135** is sensitive to air. Moreover, the triphosphine ligands in complex **134** and **135** become non-chiral when they come off from the chiral metal template. However conversion of the uncoordinated phosphorus unit in each complex to its oxide or sulfide will form a stable diphosphine chelate complex and generate a carbon chiral ligand at the same time. Indeed there is presence in the literature for the oxidation of coordinated or uncoordinated phosphino groups in phosphine metal complexes¹⁰⁸. Therefore stereoselective oxidation of complexes **134** and **135** was attempted. With direct treatment of the mixture of complexes **134** and **135** with H₂O₂, four diastereomeric mono-oxidized products **139a**, **b** and **140a**, **b** (Scheme 2.4) were produced in a ratio of 14:3:1:3, respectively. As indicated by ³¹P {¹H}NMR studies, the crude reaction product showed three sets of three doublet of a doublet resonance signals at δ [26.9 (dd, ²J_{PP} = 22.9 Hz, ³J_{PP} = 53.4 Hz), 43.8 (dd, J_{PP} = 34.3 Hz, ²J_{PP} = 22.9 Hz) and 53.5 (dd, J_{PP} = 34.3 Hz, ³J_{PP} = 53.4 Hz)], δ [28.1 (dd, ²J_{PP} = 15.3 Hz, ³J_{PP} = 42.0 Hz), 34.8 (dd, J_{PP} = 34.3 Hz, ³J_{PP} = 42.0 Hz) and 67.9 (dd, J_{PP} = 34.3 Hz, ²J_{PP} = 15.3 Hz)] and δ [28.7 (dd, ²J_{PP} = 15.3 Hz, ³J_{PP} = 34.3 Hz), 45.7 (dd, J_{PP} = 30.5 Hz, ²J_{PP} = 15.3 Hz) and 55.0 (dd, J_{PP} = 30.5 Hz, ³J_{PP} = 34.3 Hz)], which were assigned to complexes **139a**, **b** and **140a** respectively; together with a set of two doublet and one singlet resonance signals at δ [30.2, 40.6 (d, J_{PP} = 26.7 Hz) and 72.8 (d, J_{PP} = 26.7 Hz)], which was assigned to complex **140b**. The NMR assignment between diastereomers (**139** and **140**) was based on the re-coordination of liberated ligand (*R*)-**142** to *S*- and *R*-template respectively (Scheme 2.5), which will be discussed later. The NMR assignment between regioisomers (**139a** and **139b**; **140a** and **140b**) was based on the comparison with their sulfide analogues, which will be discussed in 2-2.3.

Scheme 2.4

It should be noted that complex **139a** is the direct oxidized product of complex **134a**. The product ratio for complex **139a** (67%) is slightly higher than that of complex **134a** (63%) in the original equilibrium mixture. This indicated that even though the oxidation process might be fast by using H_2O_2 as oxidizing reagent, it was still possible for the other three diastereomers (**134b**, **135a**, **135b**) to isomerize to complex **134a** before they were being oxidized. The relationship within complexes **139** and **140** is the same as their precursors **134** and **135**. However the isomerization process could only occur between two regioisomers such as between **139a** and **139b** or between **140a** and **140b**, since the carbon chirality of the oxidized products is fixed. Attempt to crystallize out any of the four diastereomers in pure form was unsuccessful. Although the major diastereomer **139a** could be obtained in relatively pure form by silica column chromatography, the isolation process was inefficient as it would readily isomerize to its regioisomer **139b** in solution.

In the oxidation process, the stereoselectivity was not affected significantly by different experimental conditions. The change of solvent from dichloromethane to chloroform, acetonitrile or methanol led to only minor variations in the product selectivity. Different reaction temperatures (-5 , 25 , 40 or 61 $^{\circ}\text{C}$) also did not affect the selectivity of the product formation. Apart from hydrogen peroxide, other oxidizing reagents such as

tert-butyl hydroperoxide were also used to oxidize complexes **134** and **135**. However they showed similar stereoselectivity. On the other hand, oxygen gas was found to oxidize the mixture of **134** and **135** very slowly at room temperature as only about 5% of the oxidized product was formed after two days. However the use of potassium permanganate or iodine as the oxidants generated a complex mixture of yet unidentified compounds, with only a trace amount of expected products.

The crude diastereomeric product mixture of **139** and **140** was subsequently treated with conc. hydrochloric acid (Scheme 2.4) for the chemoselective removal of the naphthylamine auxiliary, to generate an enantiomerically enriched mixture of dichloro complexes **141** [enriched in (*S*)-**141**]. After repeated crystallization, neutral dichloro complex (*S*)-**141** was isolated in its enantiomerically pure state as yellow crystals in 40% yield, mp 331-333 °C (decomp.), $[\alpha]_D +89^\circ$ (*c* 0.1 CH₂Cl₂). The ³¹P {¹H}NMR spectrum of the crystallized product in CD₂Cl₂ exhibited three doublet of a doublet resonance signals at δ 24.6 (dd, ³*J*_{PP} = 21.0 Hz, ²*J*_{PP} = 66.8 Hz), 55.2 (dd, *J*_{PP} = 11.4 Hz, ²*J*_{PP} = 66.8 Hz) and 70.4 (dd, *J*_{PP} = 11.4 Hz, ³*J*_{PP} = 21.0 Hz). The molecular structure and absolute configuration of (*S*)-**141** were subsequently confirmed by X-ray crystallography (Figure 2.2), and selected bond lengths and angles are given in Table 2.2. The structural analysis affirmed that a five-membered diphosphine chelate with a dangling diphenylphosphinyl group was formed, and the newly formed stereogenic centre at *C*₂ was established to adopt the *S* absolute configuration. The five-membered diphosphine chelate adopts the λ ring conformation, with the phosphine oxide substituent at *C*₂ occupying the sterically favorable equatorial position. The geometry at palladium(II) is slightly distorted square plane with a distortion angle of 5.2° and a mean deviation from planarity of 0.013 Å. The intraligand angles at the palladium(II) atom are P₁-Pd-P₂ 84.7(1)° and Cl₁-Pd-Cl₂ 91.5(1)° and the interligand angles were Cl₁-Pd-P₁ 92.4(1)° and Cl₂-Pd-P₂ 91.2(1)°. The geometry at P₃ is distorted tetrahedral with angles in the range of 104.4(2)° to 113.2(2)° and the distortion is resulted mostly by the

P₃-O₁ double bond. This molecular has two Pd-Cl linkagens with the distance of Pd-Cl₁ 2.348 (1) Å and Pd-Cl₂ 2.364 (1) Å. One of the phenyl rings (C₃ to C₈) is disordered into two positions with occupancy of 60/40 separately.

Figure 2.2 Crystal Structure of Complex (*S*)-**141**

Table 2.2 Selected Bond Lengths (Å) and Angles (deg) for Dichloro Complex (*S*)-**141**

Pd(1) – P(1)	2.241(1)	P(1) – Pd(1) – Cl(2)	174.3(1)
Pd(1) – P(2)	2.235(1)	P(1) – Pd(1) – P(2)	84.7(1)
Pd(1) – Cl(1)	2.348(1)	P(2) – Pd(1) – Cl(1)	175.9(1)
Pd(1) – Cl(2)	2.364(1)	P(2) – Pd(1) – Cl(2)	91.5(1)
P(1) – C(1)	1.845(4)	Pd(1) – P(1) – C(1)	109.8(1)
P(2) – C(2)	1.869(4)	O(1)-P(3)-C(33)	112.2(2)
P(3) – C(2)	1.828(4)	O(1)-P(3)-C(2)	112.7(2)
P(3) – O(1)	1.484(3)	C(2)-P(3)-C(33)	105.6(2)
C(1) – C(2)	1.522(6)	C(27)-P(3)-C(33)	104.4(2)
P(1) – Pd(1) – Cl(1)	92.4(1)	C(27)-P(3)-C(2)	108.2(2)
O(1)-P(3)-C(27)	113.2(2)	Cl(1) – Pd(1) – C2(1)	91.2(1)

Further treatment of complex (*S*)-**141** with aqueous cyanide liberated triphosphine mono-oxide ligand (*R*)-**142** as white solid in quantitative yield, $[\alpha]_D -45^\circ$ (*c* 0.7 CHCl₃). The ³¹P {¹H}NMR spectrum of this free ligand showed three doublet of a doublet at δ -16.7 (dd, ³J_{PP} = 7.6 Hz, ³J_{PP} = 26.7 Hz), -8.8 (dd, ²J_{PP} = 76.3 Hz, ³J_{PP} = 7.6 Hz) and 34.6 (dd, ²J_{PP} = 76.3 Hz, ³J_{PP} = 26.7 Hz). The optical purity of ligand (*R*)-**142** [*i.e.* also the dichloro complex (*S*)-**141**] was confirmed by recoordination of the liberated free ligand to (*S*)-**60** and the equally available enantiomeric complex (*R*)-**60** separately. Re-complexation of (*R*)-**142** to (*S*)-**60** gave only a pair of regioisomers **139a** and **139b** (Scheme 2.5), which could undergo *cis-trans* isomerization until equilibrium between the two regioisomers was achieved¹¹⁰. The ³¹P {¹H}NMR spectrum of the re-complexation product mixture in CDCl₃ exhibited two sets of resonance signals, each consisting of three doublet of a doublet resonance signals at δ (26.9, 43.8 and 53.5) and (28.1, 34.8 and 67.9) in a ratio of 5:1, respectively. It is noteworthy that the phosphorus resonance signals for these two regioisomeric re-complexation products are identical to those recorded for the most predominant and one of the diastereomeric products (with relative abundance of 3) in the 14:3:3:1 product mixture obtained directly from the asymmetric oxidation reaction.

Recoordination of free ligand to (*R*)-**60** similarly generated only a pair of regioisomeric complexes **143a** and **143b**, which are the enantiomeric forms of **140a** and **140b** respectively. The ^{31}P $\{^1\text{H}\}$ NMR spectrum of the re-complexation product mixture in CDCl_3 showed a set of three doublet of a doublet signals at δ (28.7, 45.7 and 55.0), together with a set of two doublet and a singlet phosphorus resonance signals at δ (30.2, 40.6 and 72.8) in an equilibrium ratio of 1:3 respectively. It is noteworthy that these resonance signals for the two re-complexation products are identical to those recorded for the other two remaining diastereomeric products obtained directly from the asymmetric oxidation reaction. Importantly, since phosphorus resonance signals at δ (26.9, 43.8 and 53.5) and (28.1, 34.8 and 67.9) were not observed, this confirmed the optical purity of the liberated phosphine-phosphine oxide ligand (*R*)-**142** [and also (*S*)-**141**]. From these recoordination experiments, spectroscopic and crystallographic studies, the four stereoisomeric products generated in the chiral metal template induced asymmetric oxidation of 1,1,2-tris(diphenylphosphino)ethane have been established to be complexes **139a,b** and **140a,b** unambiguously.

Scheme 2.5

2-2.3 Oxidation of Complexes **134** and **135** with S_8 and Liberation of Enantiomerically Pure Phosphine Mono-Sulfide Ligand

The mixture of complex **134** and **135** was treated with large excess (10 equiv.) elemental sulfur as the oxidant. The reaction was monitored by the ^{31}P $\{^1\text{H}\}$ NMR spectroscopy and was found to be completed in one day. The large excess of sulfur was crucial, as there was no conversion if less than 3 equiv. of sulfur was added. Nevertheless unreacted sulfur was difficult to remove and hindered the isolation of major product **144a**. As indicated by ^{31}P $\{^1\text{H}\}$ NMR (CD_3CN) studies, four expected diastereomers (Scheme 2.5) were present in the crude product: **144a** [δ 45.4 (dd, $^2J_{\text{PP}} = 24.4$ Hz, $^3J_{\text{PP}} = 55.0$ Hz), 46.9 (dd, $J_{\text{PP}} = 33.6$ Hz, $^2J_{\text{PP}} = 24.4$ Hz) and 55.5 (dd, $J_{\text{PP}} = 33.6$ Hz, $^3J_{\text{PP}} = 55.0$ Hz)], **144b** [δ 32.7 (dd, $^2J_{\text{PP}} = 34.3$ Hz, $^3J_{\text{PP}} = 61.0$ Hz), 45.0 (dd, $J_{\text{PP}} = 22.9$ Hz, $^3J_{\text{PP}} = 61.0$ Hz) and 64.8 (dd, $J_{\text{PP}} = 22.9$ Hz, $^2J_{\text{PP}} = 34.3$ Hz)], **145a** [δ 46.1 (dd, $^2J_{\text{PP}} = 19.1$ Hz, $^3J_{\text{PP}} = 49.6$ Hz), 47.7 (dd, $J_{\text{PP}} = 34.3$ Hz, $^2J_{\text{PP}} = 19.1$ Hz) and 55.0 (dd, $J_{\text{PP}} = 34.3$ Hz, $^3J_{\text{PP}} = 49.6$ Hz)], **145b** [δ 36.3 (d, $^2J_{\text{PP}} = 22.9$ Hz), 43.1 (d, $J_{\text{PP}} = 11.4$ Hz) and 67.6 (dd, $J_{\text{PP}} = 11.4$ Hz, $^2J_{\text{PP}} = 22.9$ Hz)] in the ratio of 21:2:2.6:2, respectively. The NMR assignment of each product was based on the re-coordination of liberated ligand (*R*)-**147** to *S*- and *R*-template respectively (Scheme 2.7), which will be discussed later. It should be noted that the selectivity of the major product **144a** (77%) is higher than that of its precursor complex **134a** (63%) or its oxide analogue **138a** (67%), which means that under a slower conversion process, there are more chances for the other three equilibrium precursor complexes (**134b**, **135a** and **135b**) isomerizing to **134a** before their converting to the phosphine sulfide. The relationship within complexes **144** and **145** is the same as that of complexes **139** and **140**. Similarly the isomerization process could only occur between two regioisomers such as between **144a** and **144b** or between **145a** and **145b**.

Scheme 2.6

The large excess elemental sulfur could be removed by column chromatography and the major product was crystallized out from CH_3CN and diethyl ether as light yellow crystals in 32% yield: mp 216-217 °C (decomp.), $[\alpha]_D + 104^\circ$ (c 0.8 CH_2Cl_2). Complex **144a** was not stable in solution as it slowly isomerized to its regioisomer **144b** to form an equilibrium mixture of **144a** and **144b** in the ratio of 21:1, respectively. The single crystal X-ray analysis indicated that complex **144a** was crystallized with two crystallographically independent molecules in the asymmetric unit. However they have identical stereochemistry and differ only slightly in bond lengths and angles. For clarity, only one molecule is shown in Figure 2.3. Selected bond lengths and angles are given in Table 2.3. The structural analysis affirmed that a five-membered diphosphine chelate was formed, and the newly formed stereogenic centre at C_{16} (C_{68} for the other molecule) is established to adopt the *S* absolute configuration as expected. The five-membered diphosphine chelate adopts the λ ring conformation, with the phosphine sulfide substituent at the chiral carbon atom occupying the sterically favorable equatorial position. The geometry at palladium(II) is slightly distorted square plane with a distortion angle of 1.6° (0.6° for the other one) and a mean deviation from planarity of $0.016 \text{ \AA}$ ($0.031 \text{ \AA}$ for the other one). In this molecule, the P=S double bond is indeed formed with the distance of $1.943(4) \text{ \AA}$ ($1.945(3) \text{ \AA}$ for the other one). Interestingly one of the phenyl rings [C_{29} - C_{34}] at P_2 is locked to a position with

the proton at C₂ which is slightly protruding above the plane of naphthyl ring close to the ring. This corresponds to a multiplet proton resonance signal presenting at δ 7.02-7.10 in ¹H NMR spectrum indicating that the proton is shielded by the phenyl ring.

Table 2.3 Selected Bond Lengths (Å) and Angles (deg) for Complex (S,S)-**144a**

Pd(1) – C(1)	2.086(9)	Pd(1) – N(1)	2.160(8)
Pd(1) – P(1)	2.380(2)	Pd(1) – P(2)	2.246(2)
P(2) – C(15)	1.85(1)	P(1) – C(16)	1.85(1)
P(3) – S(1)	1.943(4)	C(15) – C(16)	1.53(1)
P(3) – C(16)	1.86(1)	C(1) – Pd(1) – N(1)	81.3(3)
C(1) – Pd(1) – P(2)	94.2(3)	N(1) – Pd(1) – P(2)	174.4(2)
C(1) – Pd(1) – P(1)	179.4(3)	N(1) – Pd(1) – P(1)	99.1(4)
P(2) – Pd(1) – P(1)	86.4(1)	P(5) – Pd(2) – P(4)	85.7(1)
Pd(2) – C(53)	2.061(8)	Pd(2) – N(2)	2.149(9)
Pd(2) – P(4)	2.394(2)	Pd(2) – P(5)	2.227(3)
P(5) – C(67)	1.833(9)	P(4) – C(68)	1.85(1)
P(6) – S(2)	1.945(3)	C(67) – C(68)	1.53(1)
P(6) – C(68)	1.853(8)	C(53) – Pd(2) – N(2)	81.2(4)
C(53) – Pd(2) – P(5)	92.8(3)	N(2) – Pd(2) – P(5)	173.8(2)
C(53) – Pd(2) – P(4)	178.4(3)	N(2) – Pd(2) – P(4)	100.4(2)

Figure 2.3 Crystal Structure of Complex (*S,S*)-144a

Upon removal of the chiral auxiliary chemoselectively (Scheme 2.7), the dichloro complex (*S*)-**146** was generated and isolated as yellow crystals in 80% yield, mp 318-319 °C, $[\alpha]_D +39^\circ$ (*c* 0.4 CH₂Cl₂). The ^{31}P $\{^1\text{H}\}$ NMR spectrum of the crystallized product in CDCl₃ exhibited three doublet of a doublet resonance signals at δ 42.7 (dd, $^2J_{\text{PP}} = 64.8$ Hz, $^3J_{\text{PP}} = 15.3$ Hz), 52.6 (dd, $J_{\text{PP}} = 11.5$ Hz, $^2J_{\text{PP}} = 64.8$ Hz) and 70.8 (dd, $J_{\text{PP}} = 11.5$ Hz, $^3J_{\text{PP}} = 15.3$ Hz).

Scheme 2.7

Further treatment of complex (*S*)-**146** with aqueous cyanide liberated the optically pure mixed phosphine-phosphine sulfide ligand (*R*)-**147** as white solid in quantitative yield, $[\alpha]_D -43^\circ$ (*c* 0.8 CHCl₃). The ^{31}P $\{^1\text{H}\}$ NMR spectrum of this free ligand in CDCl₃ showed two doublet and one doublet of a doublet at δ -17.0 (d, $^3J_{\text{PP}} = 38.2$ Hz), -9.4 (d, $^2J_{\text{PP}} = 8.2$ Hz) and 55.4 (dd, $^3J_{\text{PP}} = 38.2$ Hz, $^2J_{\text{PP}} = 8.2$ Hz). Ligand (*R*)-**147** was re-coordinated to (*S*)-**60** and gave only a pair of regioisomers **144a** and **144b** (Scheme 2.7), which could undergo *cis-trans* isomerization until an equilibrium ratio of 13:1 for **144a** and **144b**, respectively, was achieved. Re-coordination of the free ligand to (*R*)-**60** similarly generated only a pair of regioisomeric complexes **148a** and **148b**, which are the enantiomeric forms of **145a** and **145b** respectively in an equilibrium ratio of 1.7:1. Similarly the recoordination experiments

confirmed the optical purity of the liberated ligand (*R*)-**147** [and also (*S*)-**146**]. Together with spectroscopic and crystallographic studies, the four stereoisomeric products in the mixture of sulfide complexes have been established unambiguously to be complexes **144a**, **b** and **145a**, **b**.

2-2.4 Oxidation of Complexes **134** and **135** with Se

Being in the same family with oxygen and sulfur, selenium was also used to react with the free phosphine P(III) in complexes **134** and **135** (Scheme 2.8). As monitored by the ^{31}P $\{^1\text{H}\}$ NMR spectroscopy the reaction was completed in one day when excess of elemental selenium was used. However the reaction was found inefficient as the ^{31}P $\{^1\text{H}\}$ NMR studies showed that some phosphine oxide products (**139** and **140**) were generated. As indicated by ^{31}P $\{^1\text{H}\}$ NMR studies, the stereoselectivity of this selenium oxidation reaction is significantly poorer than those involving H_2O_2 and elemental sulfur. Attempts to isolate the products were not successful. It should be noted that the phosphorus selenium double bond is known to be unstable so that selenium could transfer between P(III) species by a bimolecular process¹¹⁸. Such a migration process could result in the change of chirality in the proposed product diastereomers. Thus the study on the oxidation reaction involving selenium did not proceed further.

Scheme 2.8

2-3 Conclusion

In conclusion, the chiral organopalladium complex **60** has been proved to be a good template to promote hydrophosphination between activated C-C double bond and PPh_2H . The stereochemistry of functional groups on the new chelating diphosphine ligands can be controlled efficiently by the chiral naphthyl auxiliary. Reactions in this chapter also illustrate a convenient method for asymmetric synthesis of mixed triphosphine ligands with P=O or P=S functional groups.

2-4 Experimental Section

Reactions involving air-sensitive compounds were performed under a positive pressure of purified nitrogen. Routine ^1H NMR spectroscopy were recorded at 300.1 and 500.1 MHz on a Bruker ACF or Bruker AMX 500 NMR spectrometers. ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shifts were referenced relative to SiMe_4 and H_3PO_4 , respectively. Optical rotations were measured on the specified solution in a 0.1 dm cell at 25 °C with a Perkin-Elmer Model 341 polarimeter. Melting points were determined on a Büchi melting point B-545. Elemental analyses were performed by the Elemental Analysis Laboratory of Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University .

The enantiomerically pure forms of (*S*)-**60** and (*R*)-**60** were prepared by the method reported previously¹¹¹.

Caution! *All the complexes described as perchlorate salt should be handled as potentially explosive compounds.*

Two possible pathways for generating the mixture of four diastereomers 134 and 135. Triphosphine ligand 1,1,2-tris(diphenylphosphino)ethane was synthesized by refluxing 1,1-bis(diphenylphosphino)ethene (0.616g, 1.5mmol), diphenylphosphine (0.289g, 1.5mmol) and catalytic amount of potassium *tert*-butoxide in THF (25 mL) for 2 hours¹¹⁶. After that the mixture was added to a solution of (*S*)-**60** (0.748g, 1.5mmol) in dichloromethane (20 mL) and stirred at room temperature for 1 day.

The same mixture of complexes could also be easily achieved by the reaction of stoichiometric amounts of complex (*S*)-**60**, 1,1-bis(diphenylphosphino)ethene and diphenylphosphine in dichloromethane at room temperature for 1 day.

Attempt to synthesize of [SP-4-3-dichloro{2-diphenylphosphinyl-1,1-bis(diphenylphosphino)ethane-*P*¹,*P*²}] palladium(II), 138. PdCl₂(NCMe)₂ (0.064g, 0.3mmol), 1,1-bis(diphenylphosphino)ethene (0.100g, 0.3mmol) and P(O)Ph₂H diphenylphosphine oxide (0.050g, 0.3mmol) were mixed together and stirred in dichloromethane for 2 hours. Complex **138** was crystallized out from dichloromethane and diethyl ether as colourless crystals: mp 216-217 °C; 0.166g (85% yield). Anal.Calcd for C₃₈ H₃₃ Cl₂ O P₃ Pd: C, 58.8; H, 4.3; Found C, 58.4; H, 4.0. ³¹P {¹H}NMR (CDCl₃) δ -32.5 (d, 2P, ³J = 12.3 Hz, P), 29.4 (t, 1P, ³J = 12.3 Hz, P); ¹H NMR (CDCl₃) δ 1.96-2.13 (m, 1H, CH), 4.96 (tdd, 2H, ²J_{HH} = 5.7 Hz, J_{PH} = 12.2 Hz, J_{PH} = 18.3 Hz, CH₂), 7.38-8.20 (m, 30H, aromatics).

Asymmetric oxidation reaction and removal of the naphthylamine auxiliary.

Isolation of [SP-4-3-(*S*)-dichloro {1-diphenyloxophosphinyl-1,2-bis(diphenylphosphino) ethane-*P*¹,*P*²}] palladium(II), (*S*)-141. To the mixture of

complexes **134** and **135**, 10 mL of 35% H₂O₂ was added and stirred vigorously for 1 hour. The resulting mixture (complexes **139** and **140**) was washed with distilled water to remove excess hydrogen peroxide and reacted with 15 mL conc. hydrochloric acid overnight subsequently. The resulting mixture (complexes **141**) was washed with water (3 × 40 mL) and dried with MgSO₄. After repeated recrystallization from dichloromethane and diethyl ether, optically pure (*S*)-**141** was obtained as yellow crystals: mp 331-333 °C (decomp.); [α]_D +89° (*c* 0.1, CH₂Cl₂); 0.473 g (40% yield). Anal. Calcd for C₃₈H₃₃Cl₂O P₃ Pd: C, 58.8; H, 4.3. Found: C, 58.5; H, 4.2. ³¹P {¹H} NMR (CD₂Cl₂) δ 24.6 (dd, 1P, ²J_{PP} = 21.0 Hz, ³J_{PP} = 66.8 Hz, P), 55.2 (dd, 1P, J_{PP} = 11.4 Hz, ³J_{PP} = 66.8 Hz, P) and 70.4 (dd, 1P, J_{PP} = 11.4 Hz, ²J_{PP} = 21.0 Hz, P); ¹H NMR (CD₂Cl₂) δ 2.51-2.93 (m, 2H, CH₂), 3.03-3.22 (m, 1H, CH), 7.04-8.43 (m, 30H, aromatics).

Liberation of (*R*)-1-diphenyloxophosphinyl-1,2-bis(diphenylphosphino)ethane, (*R*)-142**** A solution of (*S*)-**141** (0.072g, 0.1mmol) in dichloromethane (30 mL) was stirred vigorously with a saturated aqueous solution of potassium cyanide (2 g) for 2 hours. The organic layer was separated, washed with water (3 x 20 mL), and dried (MgSO₄). Upon removal of the solvent, white solid was obtained: [α]_D -45° (*c* 0.7, CHCl₃); 0.053 g (95% yield). ³¹P {¹H} NMR (CDCl₃) δ -16.7 (dd, 1P, ³J_{PP} = 7.6 Hz, ³J_{PP} = 26.7 Hz, P), -8.8 (dd, 1P, ²J_{PP} = 76.3 Hz, ³J_{PP} = 7.6 Hz, P) and 34.6 (dd, 1P, ²J_{PP} = 76.3 Hz, ³J_{PP} = 26.7 Hz, P); ¹H NMR (CDCl₃) δ 2.06-2.22 (m, 1H, CH₂), 2.51-2.69 (m, 1H, CH₂), 3.02-3.18 (m, 1H, CH₁), 6.62-7.72 (m, 30H, aromatics).

Typical procedure used for the re-complexation reactions. Stoichiometric amounts of complex (*S*)-**60** or (*R*)-**60** and free ligand [either (*R*)-**142** or (*R*)-**147**] were stirred in dichloromethane separately at room temperature and the solution was monitored by ³¹P {¹H} NMR spectroscopy until equilibrium was established.

Selective conversion of P(III) to P=S and isolation of [SP-4-4-{(S)-1-[1-(dimethylamino)ethyl] naphthyl- C^2 , N} {(S)-1-diphenylthiophosphinyl-1,2-bis(diphenylphosphino) ethane- P^1, P^2 }] palladium(II) perchlorate, **144a.** Complex (S)-**60** (1.072g, 2.2 mmol), 1,1-diphenylphosphinoethene (0.892g, 2.2mmol) and diphenylphosphine (0.419g, 2.2mmol) were stirred for 2 hours in dichloromethane (30 mL) followed by adding excess elemental sulfur (0.424g). The mixture was allowed to be stirred overnight before separation by column chromatography. After chromatographic purification, complex **144a** was crystallized from acetonitrile and diethyl ether as light yellow crystals: mp 216-217 °C (decomp.), $[\alpha]_D +104^\circ$ (*c* 0.8 CH₂Cl₂); 0.719g (32% yield). Anal. Calcd for C₅₂ H₄₉ Cl S O₄ N P₃ Pd: C, 61.3; H, 4.8, N, 1.4. Found C, 60.8; H, 5.1, N 0.9. ³¹P {¹H}NMR (CD₃CN) δ [45.4 (dd, 1P, ²*J*_{PP} = 24.4 Hz, ³*J*_{PP} = 55.0 Hz, P), 46.9 (dd, 1P, *J*_{PP} = 33.6 Hz, ²*J*_{PP} = 24.4 Hz, P) and 55.5 (dd, 1P, *J*_{PP} = 33.6 Hz, ³*J*_{PP} = 55.0 Hz, P)]; ¹H NMR (CD₃CN) δ 1.78 (d, 3H, ³*J*_{HH}=6.5Hz, CHMe), 2.10 (d, 3H, ⁴*J*_{PH}=0.6Hz, NMe_{ax}), 2.25 (dd, 3H, ⁴*J*_{PH}=1.5Hz, ⁴*J*_{PH}=1.3Hz, NMe_{eq}), 2.72-2.91 (m, 2H, CHCH₂), 3.25-3.31 (m, 1H, CHCH₂), 4.45 (dq, 1H, ²*J*_{HH}=⁴*J*_{PH}=6.2Hz, CHMe), 7.01-8.13 (m, 36H, aromatics).

Removal of chiral auxiliary and isolation of [SP-4-3-(S)-dichloro {1-diphenylthiophosphinyl-1,2-bis(diphenylphosphino) ethane- P^1, P^2 }] palladium(II), (S)-146**.** To the solution of **144a** (0.521g, 0.5mmol) in dichloromethane (30 mL), conc. hydrochloric acid (15ml) was added and the resulting mixture was allowed to be vigorously stirred over night before being washed with distilled water (3x30 mL). The organic layer was dried using MgSO₄, the solution filtered and diethyl ether added to give optically pure (S)-**146** as yellow crystals: mp 318-319 °C (decomp.). $[\alpha]_D +39^\circ$ (*c* 0.4 CH₂Cl₂); 0.324g (80% yield). Anal. Calcd for C₃₈ H₃₃ Cl₂ S P₃ Pd: C, 57.6; H, 4.2. Found C, 57.2; H, 3.9. ³¹P {¹H}NMR (CDCl₃) δ 42.7 (dd, 1P, ³*J*_{PP}=15.3Hz, ²*J*_{PP}=64.8Hz, P), 52.6 (dd, 1P, *J*_{PP}=11.5Hz, ²*J*_{PP}=64.8Hz, P), 70.8 (dd, 1P, *J*_{PP}=11.5Hz, ³*J*_{PP}=15.3Hz, P); ¹H NMR (CDCl₃) δ 2.50-2.53

(m, 2H, CH_2), 3.00-3.20 (m, 1H, CH), 6.90-8.10 (m, 30H, aromatics).

Liberation of (R)-1-diphenylthiophosphinyl-1,2-bis(diphenylphosphino)ethane, (R)-147. A solution of (*S*)-**146** (0.040g, 0.05mmol) in dichloromethane (30 mL) was stirred vigorously with a saturated aqueous solution of potassium cyanide (1g) for 1 hour. The resulting colourless organic layer was separated, washed with water, and dried with MgSO_4 . Upon removal of solvent, a white solid was obtained: $[\alpha]_{\text{D}} -42.9^\circ$ (*c* 0.8 CHCl_3); 0.030g (95% yield). ^{31}P { ^1H }NMR (CDCl_3) δ -17.0 (d, 1P, $^3J_{\text{PP}}=38.2\text{Hz}$, P), -9.4 (d, 1P, $^2J_{\text{PP}}=8.2\text{Hz}$, P), 55.4 (dd, 1P, $^2J_{\text{PP}}=8.2\text{Hz}$, $^3J_{\text{PP}}=38.2\text{Hz}$, P); ^1H NMR (CDCl_3) δ 1.83-2.28 (m, 2H, CH_2), 2.40-2.54 (m, 1H, CH), 6.50-7.77 (m, 30H, aromatics).

Preparation of the mixture of complexes 149 and 150. Complex (*S*)-**60** (0.183g, 0.4 mmol), 1,1-diphenylphosphinoethene (0.149g, 0.4mmol) and diphenylphosphine (0.070g, 0.4 mmol) were stirred for 2 hours followed by adding excess elemental selenium (0.147g). The mixture was allowed to be stirred for overnight before filtration of unreacted selenium solid.

Crystal structure determination of (S)-141. The structure was analyzed at the National University of Singapore using a Siemens SMART CCD diffractometer with graphic monochromated Mo $\text{K}\alpha$ radiation. SADABS absorption correction was applied. The absolute configuration of these complexes was determined unambiguously using the Flack parameter¹¹². Hydrogen atoms were introduced at fixed distance from carbon atoms and were assigned fixed thermal parameters.

Crystal structure determination of 138 and 144a. The structure of complexes **138** and **144a** was analyzed at Nanyang Technological University using a Bruker Kappa Apex II CCD diffractometer with graphic monochromated Mo $\text{K}\alpha$ radiation. Absorption corrections were made using Semi-empirical from equivalents. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The absolute

configuration of the complex **144a** was determined unambiguously using the Flack parameter¹¹². All non-hydrogen atoms were refined anisotropically while all hydrogen atoms were introduced at fixed distance from carbon (and nitrogen) atoms and were assigned fixed thermal parameters.

CHAPTER

3

CHEMOSELECTIVE AND STEREOSELECTIVE OXIDATION OF TRIPHOSPHINE LIGAND CONTAINING A P-STEREOGENIC CENTRE

3-1 Introduction

Enantiomerically pure bidentate phosphine ligands have been regarded as powerful chiral auxiliaries in asymmetric catalysis¹⁰⁶. A vast majority of this kind of compounds have diphenylphosphino donor group, while the chirality of each ligand usually comes from the carbon-backbone. On the contrary, only few examples of optically active bidentate phosphines ligands containing stereogenic phosphorus donor atoms have been reported⁶⁶. Tedious synthetic routes via the protected form of phosphine oxides, phosphine sulfides, phosphonium salts, and phosphine-borane adducts etc, make the P-chiral bidentate phosphine ligands receive far less attention in the field of enantioselective catalysis. Until the introducing of an optically active orthometallated amine to the resolution strategies, a significant development has been achieved for the preparation of such kind of bidentate phosphine ligands³¹.

As mentioned in Chapter 1, Wild³¹ has reviewed the resolution of many racemic bidentate phosphine ligands firstly involving the preparation of a pair of diastereomeric palladium complexes as their chloride salts and subsequently replacement of the chloride with a PF_6^- counter ion. This anionic exchange process is to facilitate the subsequent fractional crystallization process. For example, resolution of

($\pm$)-1-(diphenylphosphino)-2-(methylphenylphosphino) benzene^{38b}, with a chiral palladium complex (*S*)-**18** (Scheme 1.32) produced two diastereomeric complexes. The chloride salts were then converted into their PF₆⁻ analogues in high yield. One diastereomer (*S,Rp*)-**48** was crystallized efficiently in its enantiomerically pure form from the diastereomeric mixture. On the other hand, resolution of ($\pm$)-1-(diphenylphosphino)-2-(methylphenylphosphino) ethane^{38c}, with a chiral palladium complex (*R*)-**20** (Scheme 1.33) initially produced four diastereomeric chloride salts, which were converted into their PF₆ derivatives. Fractional crystallization gave a mixture of regioisomeric complexes (*R,Rp*)-**50** and (*R,Rp*)-**51**, which both contain *S* form of the ligand. Attempts to isolate one single diastereomer (*R,Rp*)-**51** from the mixture of regioisomeric complexes (*R,Rp*)-**50** and (*R,Rp*)-**51** were found inefficient. From a comparison of these two resolution experiments, it is clear that, with the increase of the number of diastereomers, it will be more difficult to isolate one single pure diastereomer in the resolution processes. Interestingly the asymmetric reaction discussed in this chapter involved production of a mixture of five diastereomers. But only one single diastereomer could be isolated efficiently.

3-2 Results and Discussion

3-2.1 Isolation and Characterization of Complex (*S,S,Sp*)-**152a**

When treated with H₂O₂, all of the three free phosphorus units in the racemic triphosphine ligand, 1-bis(diphenylphosphino)-2-(ethylphosphino)ethane ($\pm$)-**151** were oxidized to their phosphine oxides. Upon coordination to the chiral palladium(II) complex (*S*)-**60**, only one phosphine unit in ($\pm$)-**151** would be oxidized to phosphine oxide as two of the diphenylphosphino units in the ligand formed a five-membered chelate to the palladium(II) centre leaving one free phosphine dangling unprotected. This asymmetric oxidation was conducted by coordination of the free ligand ($\pm$)-**151** with (*S*)-**60** followed by

treatment of the complex solution with H_2O_2 . As illustrated in Scheme 3.1, theoretically, up to eight diastereomeric oxidized products could be produced in this asymmetric oxidation process. The diastereomers labeled as a pair of **na** and **nb** (**n** = **152-155**) were regioisomers. Both possess the same absolute configurations at the newly formed stereogenic carbon and phosphorus centres. Diastereomers, **152** and **153** have the same *S* configuration at their phosphorus centres but with opposite configuration at the newly formed carbon stereogenic centres. Similarly diastereomers labeled as **154** and **155** have the same *R* configuration at their phosphorus centres but opposite absolute configuration at the carbon stereogenic centres. Due to the strong electronic and steric effect of the chiral naphthylamine auxiliary, these eight possible diastereomers do not exist in equal amount in the actual oxidation reaction mixture. Only five distinct isomeric products were detected in the ^{31}P $\{^1\text{H}\}$ NMR spectrum with an integration ratio of 8:1:2:2.5:3.

Scheme 3.1

Alternatively, the same diastereomeric mixture of monoxidized diastereomers could also be prepared via the nucleophilic addition reaction between the coordinated 1,1-bis(diphenylphosphino)ethylene and ($\pm$)-ethylphenylphosphine, followed by treatment with hydrogen peroxide (Scheme 3.2). Due to the activation of the double bond by the coordination of the palladium(II) centre, the addition of ($\pm$)-ethylphenylphosphine was smoothly carried out at room temperature. Transitional complex **156** containing a four-membered chelate ring isomerized completely to the more stable five-membered chelates within a day, which could be subsequently oxidized to give the mixture of monoxide products.

Scheme 3.2

The major isomer in the diastereomeric mixture was isolated efficiently by crystallization as yellow prisms from dichloromethane and diethyl ether, $[\alpha]_{\text{D}} +117^\circ$ (*c* CH_2Cl_2) in 41% yield. Its molecular structure and absolute configuration were subsequently revealed by X-ray crystallography (Figure 3.1) and found to be (*S,S,S*_p)-**152a** (Scheme 3.1). Selected bond lengths and angles are given in Table 3.1. The structural analysis affirmed that a five-membered diphosphine chelate with a dangling diphenylphosphinyl oxide group is formed, and the newly formed stereogenic centres at C_{24} and P_1 adopt *S* and *S*_p absolute configurations, respectively. In addition, the five-membered diphosphine chelate adopts the λ ring conformation, with the phosphine oxide substituent at C_{24} occupying the sterically favorable equatorial position. The square planar coordination geometry of the palladium(II) centre is slightly distorted by the stereochemical constraints

of the chelating ligands and the methyl substituents on the nitrogen donor with a distortion angle of 4.4° and a mean deviation from planarity of $0.045 \text{ \AA}$. The geometry at P_3 is distorted tetrahedral with angles in the range of $104.2(3)^\circ$ to $114.8(2)^\circ$. The ethylphenylphosphino moiety was located *trans* to the nitrogen atom of the chiral auxiliary. Such an arrangement was also observed in similar palladium(II) complexes³⁸ containing the chiral naphthyl amine auxiliaries and a dissymmetric diphosphine ligands. The phenyl ring (C_{17} - C_{22}) is locked to a position with the hydrogen atom at C_3 (Figure 3.1), which is slightly above the plane of naphthyl ring protruding to the ring. The significant difference in distances between the two Pd-P bonds [Pd- P_1 $2.236(1) \text{ \AA}$ and Pd- P_2 $2.370(2) \text{ \AA}$] was mainly due to the *trans* effect¹²¹ and the differing basicities of the phosphorus donors^{38b}.

Figure 3.1 Crystal Structure of Complex (*S,S*,*Sp*)-**152a**

Table 3.1 Selected Bond Lengths (Å) and Angles (deg) for Complex (*S,S,Sp*)-**152a**

Pd(1)-C(2)	2.047(5)	Pd(1)-N(1)	2.151(4)
Pd(1)-P(1)	2.236(1)	Pd(1)-P(2)	2.370(2)
P(1)-C(17)	1.812(5)	P(1)-C(16)	1.819(5)
P(1)-C(23)	1.820(5)	P(2)-C(37)	1.813(5)
P(2)-C(43)	1.818(6)	P(2)-C(24)	1.853(5)
P(3)-O(1)	1.461(4)	P(3)-C(25)	1.803(6)
P(3)-C(31)	1.815(6)	P(3)-C(24)	1.833(5)
C(2)-Pd(1)-N(1)	80.1(2)	C(2)-Pd(1)-P(1)	94.3(2)
N(1)-Pd(1)-P(1)	173.8(1)	C(2)-Pd(1)-P(2)	176.9(2)
N(1)-Pd(1)-P(2)	100.3(1)	P(1)-Pd(1)-P(2)	85.4(1)
C(17)-P(1)-C(16)	107.0(2)	C(17)-P(1)-C(23)	103.0(2)
C(16)-P(1)-C(23)	104.7(3)	C(17)-P(1)-Pd(1)	114.9(2)
C(16)-P(1)-Pd(1)	117.9(2)	C(23)-P(1)-Pd(1)	107.9(2)
C(37)-P(2)-C(43)	106.7(3)	C(37)-P(2)-C(24)	108.9(2)
C(43)-P(2)-C(24)	109.1(3)	C(37)-P(2)-Pd(1)	115.1(2)
C(43)-P(2)-Pd(1)	114.2(2)	C(24)-P(2)-Pd(1)	102.6(2)
O(1)-P(3)-C(25)	110.9(3)	O(1)-P(3)-C(31)	113.1(3)
C(25)-P(3)-C(31)	106.7(3)	O(1)-P(3)-C(24)	114.8(2)
C(25)-P(3)-C(24)	104.2(3)	C(31)-P(3)-C(24)	106.3(3)

The ^{31}P $\{^1\text{H}\}$ NMR spectrum of the isolated complex (*S,S,Sp*)-**152a** in CDCl_3 were consistent with the presence of a single diastereomer in solution by exhibiting only three doublet of a doublet at δ 27.2 (dd, 1P, $^2J_{\text{PP}}=22.9\text{Hz}$, $^3J_{\text{PP}}=53.4\text{Hz}$), 45.3 (dd, 1P, $J_{\text{PP}}=34.3\text{Hz}$, $^2J_{\text{PP}}=22.9\text{Hz}$) and 61.5 (dd, 1P, $J_{\text{PP}}=34.3\text{Hz}$, $^3J_{\text{PP}}=53.4\text{Hz}$). In the ^1H NMR spectrum (CDCl_3), one doublet of a triplet resonance signal appeared at δ 1.22, which was assigned to the methyl protons at the chiral phosphorus centre as viewed as a large P-H coupling at 21.3

Hz. On the other side, one triplet resonance signal appeared at δ 1.22 in $^1\text{H} \{^{31}\text{P}\}$ spectrum (selectively decoupled at δ_{P} 61.5) indicating that the chiral phosphorus atom exhibited a resonance signal at δ 61.5 in $^{31}\text{P} \{^1\text{H}\}$ NMR spectrum. Based on their chemical shift, the remaining two resonance signals in the $^{31}\text{P} \{^1\text{H}\}$ NMR spectrum were assigned to phosphine oxide and the phosphorus atom *trans* to naphthyl ring respectively.

3-2.2 Liberation of Ligand (*R,Rp*)-**158** and Establishment of Complexes **152** and **154**

As part of the process to liberate the chiral phosphine oxide, the naphthylamine auxiliary of the isolated complex (*S,S,Sp*)-**152a** was removed chemoselectively by treatment with conc. hydrochloric acid (Scheme 3.3) to generate a neutral dichloro complex (*S,Sp*)-**157** in 90% yield. The $^{31}\text{P} \{^1\text{H}\}$ NMR spectrum of (*S,Sp*)-**157** in CD_2Cl_2 exhibited three doublet of a doublet resonance signals at δ 24.6 (dd, $^2J_{\text{PP}}=19.1\text{Hz}$, $^3J_{\text{PP}}=64.8\text{Hz}$), 65.0 (dd, $J_{\text{PP}}=11.4\text{Hz}$, $^2J_{\text{PP}}=19.1\text{Hz}$), 70.5 (dd, $J_{\text{PP}}=11.4\text{Hz}$, $^3J_{\text{PP}}=64.8\text{Hz}$). Treatment of complex (*S,Sp*)-**157** with aqueous cyanide liberated the optically pure triphosphine mono-oxide ligand (*R,Rp*)-**158** as a white solid in quantitative yield, $[\alpha]_{\text{D}} -118^\circ$ (*c* 0.5 CH_2Cl_2). The $^{31}\text{P} \{^1\text{H}\}$ NMR spectrum of this free ligand showed three doublet of a doublet at δ -20.1, -10.0 and 35.1. Its optical purity was proven by recomplexation reaction to the *S*- and *R*-form template respectively (Scheme 3.4). Re-complexation of (*R,Rp*)-**158** to (*S*)-**60** gave only a pair of regioisomers **152a** and **152b**. The $^{31}\text{P} \{^1\text{H}\}$ NMR spectrum of the re-complexation product mixture in CDCl_3 exhibited two sets of resonance signals, each consisting of three doublet of a doublet resonance signals at δ 27.2, 45.3, 61.5 and δ 27.6 (dd, $^3J_{\text{PP}} = 45.8\text{ Hz}$, $^2J_{\text{PP}} = 19.1\text{ Hz}$), 30.9 (dd, $J_{\text{PP}} = 34.3\text{ Hz}$, $^3J_{\text{PP}} = 45.8\text{ Hz}$) and 68.6 (dd, $J_{\text{PP}} = 34.3\text{ Hz}$, $^2J_{\text{PP}} = 19.1\text{ Hz}$). It is noteworthy that these resonance signals for the two re-complexation products are identical to those that exhibit the 8 : 1 relative intensities in the diastereomeric products obtained directly from the asymmetric oxidation reaction, respectively. Re-complexation of

the liberated free ligand to (*R*)-**60** similarly generated only a pair of regioisomeric complexes **159a** and **159b**, which are the enantiomeric forms of **154a** and **154b** correspondingly. The ^{31}P $\{^1\text{H}\}$ NMR spectrum of the re-complexation product mixture in CDCl_3 showed a set of three doublet of a doublet resonance signals at δ 28.5 (dd, $^2J_{\text{PP}} = 19.1$ Hz, $^3J_{\text{PP}} = 42.0$ Hz), 47.1 (dd, $J_{\text{PP}} = 34.3$ Hz, $^2J_{\text{PP}} = 19.1$ Hz) and 58.3 (dd, $J_{\text{PP}} = 34.3$ Hz, $^3J_{\text{PP}} = 42.0$ Hz), together with a set of two doublet and one singlet phosphorus resonance signals at δ 37.5 (d, $J_{\text{PP}} = 26.7$ Hz), 70.0 (d, $J_{\text{PP}} = 26.7$ Hz) and 31.9. It is noteworthy that these resonance signals for the two re-complexation products are identical to those that exhibit the 2 : 2.5 relative intensities in the diastereomeric products obtained directly from the asymmetric oxidation reaction, respectively. Importantly, phosphorus resonance signals at δ (27.2, 45.3 and 61.5) and (27.6, 30.9 and 68.6) were not observed confirming the optical purity of the liberated triphosphine mono-oxide ligand (*R,Rp*)-**158** [and also (*S,Sp*)-**157**].

Scheme 3.3

Scheme 3.4

The re-complexation reaction not only confirmed the optical purity of the liberated ligand, it also provided spectroscopic evidence to establish the fact that the diastereomeric complexes **152a**, **152b** and **154a**, **154b** (the enantiomeric forms of **159a** and **159b** separately) were indeed formed during the asymmetric oxidation reaction since the phosphorus resonance signals for above two sets of regioisomeric re-complexation products could be discerned from those of the diastereomeric mixture obtained directly from the asymmetric oxidation reaction. However the fifth oxidized product in the crude diastereomeric mixture obtained from the selective oxidation process (Scheme 3.1), which exhibited 3 in the relative ratio, could not be unambiguously identified.

3-2.3 Attempts to Synthesize P-N Hetero Ligand

The synthesis of the P-N hetero ligand **160** was achieved by the activation of the C-C double bond in 1,1-bis(diphenylphosphino)ethene with LDA and benzyl amine (Scheme 3.5). The hetero ligand was subsequently coordinated to the chiral template (*S*)-**60** and then treated with H₂O₂. The ³¹P {¹H}NMR spectrum of the crude reaction product showed a mixture of products. Attempts to separate the product mixture were not successful. Therefore the naphthyl auxiliary was removed via acid treatment.

Scheme 3.5

Upon removal of the chiral auxiliary, yellow crystals were obtained from dichloromethane and diethyl ether. The single crystal X-ray analysis indicated that the product is complex **161**, which is centro-symmetric containing both enantiomers (RR_N and SS_N). There are two crystallographically independent molecules in the lattice differing only slightly in bond lengths and angles with the diphenyl phosphinyl substituent at the chiral carbon centre adopting sterically favorable equatorial position. For clarity, only one molecule is shown in Figure 3.2 and it has S, S_N at the stereogenic centres. Selected bond lengths and angles are given in Table 3.2. The geometry at palladium(II) is slightly distorted square plane with a distortion angle of 5.9° (4.1° for the other one) and a mean deviation from planarity of $0.068 \text{ \AA}$ ($0.047 \text{ \AA}$ for the other one). In this molecule, the Pd-N bond is indeed formed with the distance of $2.076(5) \text{ \AA}$ [$2.084(5) \text{ \AA}$ for the other one].

It was found that the nitrogen stereogenic centre is not stable in solution as the hydrogen atom is too small to act as hindrance, so that it will invert to the opposite configuration (RS_N and SR_N) rapidly. The $^{31}\text{P} \{^1\text{H}\}$ NMR spectrum of pure **161** in CDCl_3 showed two broad peaks at δ 21.3 and 63.4; while that in CD_2Cl_2 showed two sets of two broad peaks at δ 21.4, 62.4 and 26.9 and 55.4 in the ratio of 3:1. However the spectrum in THF-d_4 showed two sets of two doublet of a doublet resonance signals at δ 20.3, 63.1 ($^2J_{\text{PP}} = 28.6 \text{ Hz}$) and δ 23.4, 57.9 ($^2J_{\text{PP}} = 19.1 \text{ Hz}$) in the ratio of 5:1. As the hydrogen atoms at the nitrogen stereogenic centres formed hydrogen bonds with THF-d_4 , which hindered the inversion of the absolute configuration of nitrogen stereogenic centres, clear resonance signals were observed by $^{31}\text{P} \{^1\text{H}\}$ NMR spectroscopy. Unfortunately a racemic product was obtained in this asymmetric oxidation reaction. Attempts to separate the two enantiomers of complex **161** were not successful. Thus further study on this reaction did not proceed.

Figure 3.2 Crystal Structure of Complex **161**

Table 3.2 Selected Bond Lengths (Å) and Angles (deg) for Dichloro Complex **161**

Pd(1)-N(1)	2.076(5)	Pd(1)-P(1)	2.210(2)
Pd(1)-Cl(1)	2.281(2)	Pd(1)-Cl(2)	2.397(2)
Pd(1)-N(2)	2.084(5)	Pd(2)-P(3)	2.200(2)
Pd(2)-Cl(3)	2.300(2)	Pd(2)-Cl(4)	2.377(2)
P(1)-C(1)	1.859(6)	P(2)-C(1)	1.830(6)
P(2)-O(1)	1.488(4)	P(3)-C(34)	1.851(6)
P(4)-C(34)	1.846(5)	P(4)-O(2)	1.480(4)
C(2)-Pd(1)-N(1)	85.5(2)	N(1)-Pd(1)-Cl(1)	175.4(2)
Cl(1)-Pd(1)-P(1)	90.1(1)	N(1)-Pd(1)-Cl(2)	91.6(2)
P(1)-Pd(1)-Cl(2)	173.5(1)	Cl(1)-Pd(1)-Cl(2)	93.0(1)
N(2)-Pd(2)-P(3)	85.6(2)	N(2)-Pd(2)-Cl(3)	175.6(2)
P(3)-Pd(2)-Cl(3)	92.5(1)	N(2)-Pd(2)-Cl(4)	91.1(2)
P(3)-Pd(2)-Cl(4)	176.6(1)	Cl(3)-Pd(2)-Cl(4)	90.9(1)

3-3 Conclusion

In this chapter, preparation of a triphosphine mono-oxide ligand containing both chiral *P* and *C* centres was demonstrated. It was proved that the chiral palladium(II) template played an important role not only in the resolution step but also in the asymmetric oxidation step. Although the attempt to isolate enantiomerically pure P-N hetero ligand was unsuccessful, we believe that the synthetic route used in Chapters 2 and 3 can be used as a general strategy for the preparation of other similar P-hetero chelating ligands.

3-4 Experimental Section

Resolution of ligand (±)-151 by a chiral palladium template followed by oxidation reaction. Isolation of [SP-4-4- {(S)-1-[1-(dimethylamino)ethyl] naphthyl-C²,N} {(S)-1-(diphenylphosphino) -1-diphenylphosphinyl-2-(S)-

(ethylphenylphosphino) ethane- P^1,P^2] palladium(II) perchlorate, (S,S,Sp)-152a.

Triphosphine ligand ($\pm$)-**151** was synthesized by refluxing a mixture of 1,1-bis(diphenylphosphino)ethene (0.849g, 2.1mmol), ($\pm$)-ethylphenylphosphine (0.296g, 2.1mmol) and catalytic amount of potassium *tert*-butoxide in THF (25 mL) for 2 hours. The crude product was then added into a solution of (S)-**60** (1.01g, 2.1mmol) in dichloromethane (20 mL) and the resulting solution was stirred at room temperature for one day followed by addition of an aqueous hydrogen peroxide solution (35%, 10 mL). After being stirred vigorously for 1 hour, the mixture was washed with water (3 x 40 mL), dried with $MgSO_4$ and solvent was removed leaving a yellow powder. Crystallization of the crude product from dichloromethane and diethyl ether precipitated (S,S,Sp)-**152a** as yellow crystals, yield 0.809g (41%): mp 335-336 °C (decomp.). $[\alpha]_D +117^\circ$ (c 0.9 CH_2Cl_2);. Anal. Calcd for $C_{48}H_{49}ClO_5NP_3Pd$: C, 60.4; H, 5.2, N, 1.5. Found C, 59.9; H, 5.2, N 1.4. ^{31}P { 1H }NMR ($CDCl_3$) δ 27.2 (dd, 1P, $^2J_{PP}=22.9Hz$, $^3J_{PP}=53.4Hz$, P), 45.3 (dd, 1P, $J_{PP}=34.3Hz$, $^2J_{PP}=22.9Hz$, P) and 61.5 (dd, 1P, $J_{PP}=34.3Hz$, $^3J_{PP}=53.4Hz$, P); 1H NMR ($CDCl_3$) δ 1.22 (dt, 3H, $^3J_{HH}=7.6Hz$, $^3J_{PH}=21.3Hz$, PCH_2CH_3), 1.90 (d, 3H, $J_{HH}=6.4Hz$, $CHMe$), 2.27 (dd, 3H, $^4J_{PH}=2.9Hz$, $^4J_{PH}=3.4Hz$, NMe_{eq}), 2.36 (d, 3H, $^4J_{PH}=1.2Hz$, NMe_{ax}), 2.30-2.68 (m, 4H, CH_2 , PCH_2CH_3), 2.94-3.16 (m, 1H, CH), 4.41 (dq, 1H, $^2J_{HH}=^4J_{PH}=6.4Hz$, $CHMe$), 7.03-8.34 (m, 31H, aromatics).

Removable of naphthylamine auxiliary and isolation of [SP -4-4-(S)-dichloro {(S)-1-(diphenylphosphino)-1-diphenylphosphinyl-2-(S)-(ethylphenylphosphino) ethane- P^1,P^2] palladium(II), complex (S,Sp)-157. To a solution of (S,S,Sp)-**152a** (0.304g, 0.3mmol) in dichloromethane (50 mL), conc. hydrochloric acid (15ml) was added and the resulting mixture was vigorously stirred overnight before being washed with distilled water (3x30 mL) and dried with $MgSO_4$. Optically pure (S,Sp)-**157** was obtained as colourless crystals by crystallization of the crude powder from dichloromethane and diethyl ether, yield 0.208g (90%): mp 338-340 °C (decomp.). $[\alpha]_D +165^\circ$ (c 0.4 CH_2Cl_2);.

Anal. Calcd for $C_{34}H_{33}Cl_2O P_3 Pd$: C, 56.1; H, 4.6. Found C, 56.5; H, 5.0. $^{31}P \{^1H\}$ NMR (CD_2Cl_2) δ 24.6 (dd, 1P, $^2J_{PP}=19.1\text{Hz}$, $^3J_{PP}=64.8\text{Hz}$, P), 65.0 (dd, 1P, $J_{PP}=11.4\text{Hz}$, $^2J_{PP}=19.1\text{Hz}$, P), 70.5 (dd, 1P, $J_{PP}=11.4\text{Hz}$, $^3J_{PP}=64.8\text{Hz}$, P); 1H NMR (CD_2Cl_2) δ 1.26 (dt, 3H, $^3J_{HH}=7.6\text{Hz}$, $^3J_{PH}=21.7\text{Hz}$, PCH_2CH_3), 2.14-2.76 (m, 4H, $2CH_2$), 2.98-3.17 (m, 1H, CH), 7.02-8.38 (m, 25H, aromatics).

Liberation of (R)-1-diphenylphosphinyl-1-diphenylphosphino-2-(R)-ethylphenylphosphino ethane, ligand (R,Rp)-158. A solution of (S,Sp)-157 (0.073g, 0.1mmol) in dichloromethane (30ml) was stirred vigorously with a saturated aqueous solution of potassium cyanide (1g) for 1 hour. The colourless organic layer was separated, washed with water, and dried with $MgSO_4$. Upon removal of solvent, a white solid (R,Rp)-158 was obtained, yield 0.053g (95%): $[\alpha]_D -118^\circ$ (c 0.5 CH_2Cl_2). $^{31}P \{^1H\}$ NMR ($CDCl_3$) δ -20.1 (dd, 1P, $^3J_{PP}=26.7\text{Hz}$, $^3J_{PP}=7.6\text{Hz}$, P), -10.0 (dd, 1P, $^2J_{PP}=76.3\text{Hz}$, $^3J_{PP}=7.6\text{Hz}$, P), 35.1 (dd, 1P, $^2J_{PP}=76.3\text{Hz}$, $^3J_{PP}=26.7\text{Hz}$, P); 1H NMR ($CDCl_3$) δ 0.55 (dt, 3H, $^3J_{HH}=7.6\text{Hz}$, $^3J_{PH}=16.1\text{Hz}$, PCH_2CH_3), 0.97-1.24 (m, 2H, PCH_2CH_3), 1.71-1.87 (m, 1H, CH_2), 2.09-2.26 (m, 1H, CH_2), 2.97-3.13 (m, 1H, CH), 7.11-7.64 (m, 25H, aromatics).

Procedure for the nucleophilic addition-asymmetric oxidation pathway. Stoichiometric amounts of complex (S)-60, ($\pm$)-ethylphenylphosphine and 1,1-bis(diphenylphosphino)ethene were stirred in degassed dichloromethane at room temperature for 1 day. Subsequent asymmetric oxidation and isolation were performed as described earlier.

Attempt to synthesize racemic dichloro complex [SP-4-3-dichloro {1-diphenylphosphinyl-1-diphenylphosphino-2-benzylamino ethane- P^1,N }] palladium(II), 161. Triphosphine ligand ($\pm$) 160 was synthesized by refluxing 1,1-bis(diphenylphosphino)ethene (0.595g, 1.5mmol), benzylamine (0.238g, 1.5mmol) and catalytic amount of LDA in THF (25 mL) for 2 hours. After that the mixture was added

into a solution of (*S*)-**60** (0.729g, 1.5mmol) in dichloromethane (20 mL) and stirred at room temperature for 1 day. Aqueous hydrogen peroxide solution (35%, 10 mL) was added and stirred vigorously for 1 hour. The resulting mixture was washed with distilled water to remove excess hydrogen peroxide and reacted with 15 mL conc. hydrochloric acid overnight subsequently. The resulting mixture was washed with water (3 × 40 mL) and dried with MgSO₄. Complex **161** was isolated from dichloromethane and diethyl ether as yellow crystals: mp 228-230 °C (decomp.); 0.174 g (16% yield). Anal. Calcd for C₃₃H₃₁Cl₂N O P₂ Pd 0.25CH₂Cl₂ 0.5H₂O: C, 54.9; N, 1.9; H, 4.4. Found C, 54.8; N, 1.5; H, 4.4. ³¹P {¹H}NMR (THF, D₄) δ 20.3 (d, 1P, ²J_{PP}=28.6Hz, *P*), 23.4 (d, 1P, ²J_{PP}=19.1Hz, *P*), 57.9 (d, 1P, ²J_{PP}=19.1Hz, *P*), 63.1 (d, 1P, ²J_{PP}=28.6Hz, *P*).

Liberation of 1-diphenylphosphinyl-1-diphenylphosphino-2-benzylamino ethane, 162. A solution of **161** (0.032g, 0.05mmol) in dichloromethane (30ml) was stirred vigorously with a saturated aqueous solution of potassium cyanide (1g) for 1 hour. The colourless organic layer was separated, washed with water, and dried with MgSO₄. Upon removal of solvent, a white solid **162** was obtained, yield 0.019g (80%): [α]_D 0° (*c* 0.5 CH₂Cl₂).

Typical procedure used for the recoordination reaction. Freshly liberated ligand (*R,R*p)-**158** or **161** in dichloromethane (10ml) was transferred into each of two flasks containing stoichiometric amount of (*S*)- and (*R*)-**60** template individually. The solutions were stirred for 1 hour and ³¹P {¹H}NMR spectroscopy were used to monitor the reaction.

Crystal structure determination of (S,S,Sp)-152a, 161 The structure was analyzed at the National University of Singapore.

CHAPTER

4

CHIRAL PALLADIUM TEMPLATE INDUCED ASYMMETRIC SYNTHESIS OF BIDENTATE P-CHIRAL PHOSPHINES LIGANDS CONTAINING P(V) GROUPS

4-1 Introduction

Bisphosphine mono-oxide ligands containing both soft (P) and hard (O) Lewis base centres are powerful ligands for a variety of transition metals such as Co, Rh, IR, Pd, Ni, etc¹¹⁴. These complexes have been successfully used in many organic reactions such as hydroformylation¹¹⁵ reaction and hydrocarboxylation¹¹⁶ reaction of olefins, asymmetric cycloaddition reaction¹¹⁷, miscellaneous catalytic reaction¹¹⁸. Apart from these synthetic applications, they also play significant roles in the medicinal research¹⁰⁷ for certain types of human diseases. Similarly chiral mixed P(III) and P(V) ligands have been proved to be good catalysts in miscellaneous catalytic reactions. For example, the chiral bisphosphine mono-oxide ligand (S)-BINPO (BINPO = 2-diphenylphosphino, 2'-diphenylphosphineoxide)-binaphtyl) has been successfully used in metal catalysed Diels-Alder reaction¹⁰⁸ and nonenzymatic kinetic resolution reaction¹¹⁹. Synthesis of non-chiral bisphosphine mono-oxide ligands has been well documented¹¹⁴. On the contrary, reports on the synthesis of chiral mixed P(III) and P(V) phosphine ligands are rather rare^{120, 108}. Recently we have found that by introducing a chiral amine auxiliary stabilized

by palladium(II) centre, the synthesis of this kind of chiral ligands could be achieved efficiently^{99, 100}.

Bisphosphine mono-oxide ligands usually perform as labile metal chelates¹²¹. This could be a potential disadvantage in terms of enantioselectivity of reactions. Therefore we are interested in synthesis of chiral tridentate phosphine mono-oxide ligands. In Chapter 2 and 3, we have targeted on triphosphine ligands with prochiral carbon centres. Upon coordination of the prochiral ligand to a chiral palladium(II) template followed by selective oxidation, a chiral carbon centre could be generated in the ligand. In this Chapter, we apply this strategy to a tridentate phosphine ligand containing a prochiral phosphorus centre. In addition, the synthesis of tridentate phosphine ligands containing phosphine mono-sulfide and phosphine mono-selenide functional groups will be explored in this chapter. Furthermore, selective alkylation reaction will also be tried out in this chapter.

4-2 Results and Discussion

4-2.1 Fluxional Structure

The triphosphine ligand bis(2-diphenylphosphinoethyl)phenylphosphine $[(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{PPh}_2)]$ **163** readily displaces the two acetonitrile ligands from the chiral palladium template (*S*)-**60** to give the corresponding complex **164** (Scheme 4.1). The low-temperature (253K) ^{31}P $\{^1\text{H}\}$ NMR spectrum in CDCl_3 (Figure 4.1) of complex **164** exhibited two doublet and one doublet of a doublet resonance signals at δ -16.7 (d, $^3J_{\text{PP}} = 42.0\text{Hz}$), 42.9 (d, $J_{\text{PP}} = 26.7\text{Hz}$) and 67.5 (dd, $^3J_{\text{PP}} = 42.0\text{Hz}$, $J_{\text{PP}} = 26.7\text{Hz}$). The two downfield resonance signals at δ 42.9 and 67.5 with large coordination shift^{83, 98} and the relative upfield resonance signals at δ -16.7 are consistent with the bidentate coordination mode of the **163** ligand leaving one phosphine unit as a dangling group. The small coupling constant ($J_{\text{PP}} = 26.7\text{Hz}$) between the two coordinated phosphorus units is supportive of forming a five-membered ring^{83, 98}. These spectroscopic resonance signals indicate that the

centre and one of the terminal phosphorus units in ligand **163** are attached to palladium(II) centre while the other terminal phosphorus atom remains uncoordinated. Any coupling between the two terminal phosphorus units must be transmitted via the long carbon backbone as they are not located together in the chelate ring. Indeed, experimentally, no coupling could be observed between these two terminal phosphorus nuclei in the ^{31}P spectrum.

Scheme 4.1

When the temperature of the $^{31}\text{P} \{^1\text{H}\}$ NMR sample was raised, all the resonances became broader, indicating that the environments of all of the phosphorus nuclei were not in a static state (Figure 4.2). At room temperature three broad peaks of similar intensities were observed at δ -15.5, 42.7 and 66.6 (DMSO- d_6). These signals indicated the fluxional properties¹²² of complex **164** at room temperature. At a lower temperature (253K, Figure 4.1), the fluxional behavior of complex **164** became slower. When the temperature was increased from 300K to 363K, it was observed that the two peaks due to the two terminal phosphorus units were gradually merging, while the intensity of the peak due to the centre phosphorus atom remained the same. This is consistent with the rapid exchanging process of the two terminal phosphorus units on the NMR time scale. The system is experimentally reversible as recooling of the solution to 253K gives the same $^{31}\text{P} \{^1\text{H}\}$ NMR spectrum as the original one, indicating the five-membered chelate ring is thermodynamically favored¹²³.

Figure 4.1 VT $^{31}\text{P} \{^1\text{H}\}$ NMR Spectrum of Complex **164** in CDCl_3

Figure 4.2 VT ^{31}P $\{^1\text{H}\}$ NMR Spectrum of Complex **164** in DMSO- d_6

4-2.2 Selective Conversion of P(III) to P(V)

Ligand **163** is non-chiral. However upon coordination to a chiral template, the centre phosphorus atom of the triphosphine ligand becomes a chiral centre as the other two terminal phosphorus units are in different chemical environments. With the existence of the uncoordinated phosphorus atom, complex **164** shows a fluxional behavior. Interestingly, in a dynamic process when the ligand comes off from template, it will convert back to a non-chiral molecule. As previously reported¹¹⁰, it is possible to oxidize uncoordinated phosphine in phosphine metal complexes. The chiral cyclopalladium template induced stereoselective oxidation of complex **164** was therefore attempted with the aim of generating chiral phosphine oxide, sulfide and selenide substituent diphosphine ligands.

Direct oxidation of P(III) in complex **164** to P=O was achieved at both room temperature and a lower temperature (253K). Up to four diastereomers were generated for

each reaction. As indicated by the $^{31}\text{P} \{^1\text{H}\}$ NMR (CDCl_3) spectroscopy, four sets of resonance signals each containing one doublet of a doublet and two doublet resonance signals were exhibited at δ [31.0 (d, $^3J_{\text{PP}} = 61.0$ Hz), 42.0 (d, $J_{\text{PP}} = 26.7$ Hz) and 67.3 (dd, $J_{\text{PP}} = 26.7$ Hz, $^3J_{\text{PP}} = 61.0$ Hz)]; δ [33.0 (d, $^3J_{\text{PP}} = 42.0$ Hz), 43.3 (dd, $J_{\text{PP}} = 22.9$ Hz, $^3J_{\text{PP}} = 42.0$ Hz) and 62.3 (d, $J_{\text{PP}} = 22.9$ Hz)]; δ [33.6 (d, $^3J_{\text{PP}} = 45.8$ Hz), 42.2 (d, $J_{\text{PP}} = 22.9$ Hz) and 60.8 (dd, $J_{\text{PP}} = 22.9$ Hz, $^3J_{\text{PP}} = 45.8$ Hz)]; δ [32.4 (d, $^3J_{\text{PP}} = 38.1$ Hz), 43.5 (dd, $J_{\text{PP}} = 19.1$ Hz, $^3J_{\text{PP}} = 38.1$ Hz) and 61.6 (d, $J_{\text{PP}} = 19.1$ Hz)], which were assigned to complex **165a**, **b** and **166a**, **b** respectively. The upfield phosphorus resonance signal (31.0, 32.7, 33.6, 32.4) in each set is unambiguously assigned to phosphine oxide, while the other two downfield resonance signals with small coupling in each set are supportive of five-membered chelate in the oxidized products being intact.

Complexes **165a** and **165b** are regioisomers in which they both have *S* configuration at the newly formed *P* chiral centre, but differ in the relative regio arrangement of the four nonequivalent donor atoms on the palladium(II) centre. Similarly complexes **166a** and **166b** are regioisomers with *R* configuration at the newly generated stereogenic centre. Reaction performed at 253K produced products **165a**, **b** and **166a**, **b** in a ratio of 16.4:4.7:3.2:1 when the reaction was just completed. However the ratio of the diastereomers changed to 13:2.9:2:1 after the solution was kept at room temperature for one day. The reaction performed at room temperature produced products **165a**, **b** and **166a**, **b** in a constant ratio of 19:1.5:3:1. Therefore the different isomeric ratio was obtained when the reaction was conducted under different conditions. However the total ratio between isomers with *S* (**165a** + **165b**) and *R* (**166a** + **166b**) configurations remained the same (*ca* 5:1) in various mixtures, indicating that an isomerization process occurred between a pair of regioisomers. The major product **165a** was crystallized out efficiently from dichloromethane and diethyl ether with 62% yield, mp 205-206 °C (decomp.), $[\alpha]_{\text{D}} +79^\circ$ (*c* 0.3 CH_2Cl_2). Pure **165a** could isomerize to its regioisomer **165b** to form an equilibrium

mixture of 2.8:1 in solution.

The molecular structure and absolute configuration of (*S,S*_P)-**165a** was subsequently confirmed by X-ray crystallography (Figure 4.3). Selected bond lengths and angles are given in Table 4.1. The square planar coordination geometry of the palladium(II) atom is distorted by the stereochemical constraints between the chelating ligands and the methyl substituents on nitrogen atom with a distortion angle of 1.5° and a mean deviation of 0.002 Å. The intraligand angles at the palladium(II) atom are P₁-Pd-P₂ 84.46(5)° and N₁-Pd-C₁ 80.4(2)° and the interligand angles are N₁-Pd-P₁ 102.0(1)° and C₁-Pd-P₂ 93.2(2)°. The structure analysis affirmed that a five-membered diphosphine chelate exhibiting λ conformation with a dangling diphenylphosphinyl group was formed and the stereogenic centre at P₂ which is *trans* to the nitrogen atom of the chiral auxiliary was established to adopt the *S* absolute configuration. The phenyl ring at P₂ is locked to a position with the hydrogen atom at C₂ (Figure 4.3), which is slightly above the plane of naphthyl ring protruding in to the ring. Interestingly, this structural feature is consistent with the observation of a clear doublet of a doublet of a doublet resonance signal showed up at δ 6.82 in the ¹H NMR spectrum, indicating that the aromatic proton is shielded by the phenyl ring. On the other hand, protons at C₄₅ and C₄₈ were deshielded by P₂ as a clear doublet of a doublet of a doublet resonance signal exhibited at down field δ 8.02. In addition, the significant difference in distances between the two Pd-P bonds, Pd-P₁ 2.339(1) Å and Pd-P₂ 2.228(1) Å, is a result of the *trans* effect on the two unsymmetrical phosphorus donors. The geometry at P₃ is distorted tetrahedral with angles in the range 105.4(3)° to 113.2(3)°.

Figure 4.3 Crystal Structure of Complex (*S,S*_p)-165a

Table 4.1 Selected Bond Lengths (Å) and Angles (deg) for Complex (*S*,*Sp*)-**165a**

Pd(1)-C(1)	2.048(5)	Pd(1)-N(1)	2.125(4)
Pd(1)-P(1)	2.339(1)	Pd(1)-P(2)	2.228(1)
P(1)-C(17)	1.814(5)	P(1)-C(15)	1.842(5)
P(1)-C(23)	1.827(5)	P(2)-C(29)	1.827(5)
P(2)-C(43)	1.823(5)	P(2)-C(16)	1.837(5)
P(3)-O(1)	1.491(5)	P(3)-C(37)	1.797(7)
P(3)-C(31)	1.806(6)	P(3)-C(30)	1.808(5)
C(1)-Pd(1)-N(1)	80.4(2)	C(1)-Pd(1)-P(2)	93.2(2)
N(1)-Pd(1)-P(2)	173.5(1)	C(1)-Pd(1)-P(1)	177.4(2)
N(1)-Pd(1)-P(1)	102.0(1)	P(1)-Pd(1)-P(2)	84.5(1)
C(17)-P(1)-C(23)	108.2(2)	C(17)-P(1)-C(15)	105.9(2)
C(15)-P(1)-C(23)	102.3(2)	C(17)-P(1)-Pd(1)	115.7(2)
C(23)-P(1)-Pd(1)	117.4(2)	C(15)-P(1)-Pd(1)	105.9(2)
C(29)-P(2)-C(43)	107.6(2)	C(43)-P(2)-C(16)	103.6(2)
C(29)-P(2)-C(16)	105.9(3)	C(43)-P(2)-Pd(1)	113.1(2)
C(29)-P(2)-Pd(1)	115.6(2)	C(16)-P(2)-Pd(1)	110.1(2)
O(1)-P(3)-C(37)	113.2(3)	O(1)-P(3)-C(31)	110.8(3)
C(37)-P(3)-C(31)	107.6(3)	O(1)-P(3)-C(30)	112.8(3)
C(37)-P(3)-C(30)	105.4(3)	C(31)-P(3)-C(30)	106.6(3)

Direct oxidation of P (III) to P=S was achieved by reacting complex **164** with 1 equiv. of S₈. The reaction was found completed in one day giving complex **167a** as the major product, together with a small amount of diastereomeric complexes **167b**, and **168a**, **168b**. The less soluble product **167a** was isolated as light yellow crystals in 55% yield, mp 197-198 °C (decomp.), [α]_D +79° (*c* 0.4 CH₂Cl₂). The ³¹P {¹H}NMR spectrum of complex **167a** in CDCl₃ showed two doublet and one doublet of a doublet resonance signals at δ 42.4 (d, *J*_{PP} = 24.4Hz), 43.2 (d, ³*J*_{PP} = 61.0Hz) and 66.6 (dd, ³*J*_{pp} = 61.0Hz, *J*_{PP} = 24.4Hz). Similar to its oxide analogue (complex **165a**), complex **167a** isomerized to its regioisomer

167b in solution, giving a 3.2:1 equilibrium mixture of the two isomers. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed an additional set of doublet of a doublet and two doublet resonance signals at δ 41.6 (dd, $^3J_{\text{pp}} = 53.4\text{Hz}$, $J_{\text{pp}} = 22.9\text{Hz}$), 46.0 (d, $^3J_{\text{pp}} = 53.4\text{Hz}$) and 62.2 (d, $J_{\text{pp}} = 22.9\text{Hz}$) for the new regioisomer.

The molecular structure and absolute configuration of **167a** were subsequently confirmed by X-ray crystallography (Figure 4.4). Selected bond lengths and angles are given in Table 4.2. The geometry at palladium(II) is slightly distorted square plane with the distortion angle of 0.3° and a mean deviation from planarity of $0.004\text{ \AA}$. The intraligand angles at the palladium(II) atom are $\text{P}_1\text{-Pd-P}_2$ $84.76(5)^\circ$ and $\text{N}_1\text{-Pd-C}_2$ $80.7(2)^\circ$ and the interligand angles are $\text{N}_1\text{-Pd-P}_2$ $101.7(1)^\circ$ and $\text{C}_2\text{-Pd-P}_1$ $92.8(2)^\circ$. The structural analysis affirmed that a five-membered diphosphine chelate with a dangling diphenylphosphine sulfide group was formed. The newly formed stereogenic centre at P_1 is established to adopt the *S* absolute configuration. The five-membered diphosphine chelate adopts the λ ring conformation. The chiral phosphorus centre P_1 was found to be *trans* to the nitrogen atom of the chiral auxiliary. The phenyl ring at P_1 is locked in a position by the proton at C_3 (Figure 4.4), which is slightly above the plane of naphthyl ring protruding to the ring. Interestingly, this structure is consistent with the observation of a multiplet resonance signal at δ 6.83 in the ^1H NMR spectrum indicating that this aromatic proton was indeed shielded by the phenyl ring. On the other hand, protons at C_{2A} and C_{6A} were deshielded by P_1 as a clear doublet of a doublet resonance signal exhibited at quite down field δ 8.03. In the solid state structure, the significant difference in distances between the two Pd-P bonds [Pd-P_1 $2.228(2)\text{ \AA}$ and Pd-P_2 $2.340(2)\text{ \AA}$] is the result of the *trans* effect on the two unsymmetrical phosphorus donors. The formation of the phosphine sulfide substituent at P_3 is confirmed with bond distance of $1.948(2)\text{ \AA}$, which is significantly longer than the P=O [$1.491(5)\text{ \AA}$] in **165a**. Similarly the geometry at P_3 is distorted tetrahedral with angles in the range $104.5(3)^\circ$ to $112.9(2)^\circ$.

Figure 4.4 Crystal Structure of Complex (*S,S*_P)-**167a**

Table 4.2 Selected Bond Lengths (Å) and Angles (deg) for Complex (S,Sp)-**167a**

Pd(1)-C(2)	2.045(5)	Pd(1)-N(1)	2.140(4)
Pd(1)-P(1)	2.228(2)	Pd(1)-P(2)	2.340(2)
P(1)-C(1A)	1.800(6)	P(1)-C(17)	1.818(6)
P(1)-C(16)	1.832(6)	P(2)-C(1B)	1.812(6)
P(2)-C(1C)	1.815(6)	P(2)-C(15)	1.849(6)
P(3)-C(1D)	1.814(6)	P(3)-C(18)	1.820(5)
P(3)-C(1E)	1.828(6)	P(3)-S(3)	1.948(2)
C(2)-Pd(1)-N(1)	80.7(2)	C(2)-Pd(1)-P(1)	92.8(2)
N(1)-Pd(1)-P(1)	173.5(1)	C(2)-Pd(1)-P(2)	177.5(2)
N(1)-Pd(1)-P(2)	101.7(1)	P(1)-Pd(1)-P(2)	84.8(1)
C(1A)-P(1)-C(17)	107.5(3)	C(1A)-P(1)-C(16)	103.5(3)
C(17)-P(1)-C(16)	105.7(3)	C(1A)-P(1)-Pd(1)	114.8(2)
C(17)-P(1)-Pd(1)	115.1(2)	C(16)-P(1)-Pd(1)	109.4(2)
C(1B)-P(2)-C(1C)	108.6(3)	C(1B)-P(2)-C(15)	107.3(3)
C(1C)-P(2)-C(15)	100.7(3)	C(1B)-P(2)-Pd(1)	116.7(2)
C(1C)-P(2)-Pd(1)	116.7(2)	C(15)-P(2)-Pd(1)	105.1(2)
C(1D)-P(3)-C(18)	104.5(3)	C(1D)-P(3)-C(1E)	108.0(3)
C(18)-P(3)-C(1E)	106.2(3)	C(1D)-P(3)-S(3)	112.7(2)
C(18)-P(3)-S(3)	112.9(2)	C(1E)-P(3)-S(3)	112.1(2)

Direct oxidation of P (III) to P=Se was similarly achieved by reacting complex **164** with excess elemental selenium. The oxidation reaction was found completed in one day giving **169a** as the major product, together with a small amount of three diastereomeric complexes **169b** and **170a, b**. The major product **169a** was isolated as light yellow crystals in high yield (90%), mp 217-218 °C (decomp.), $[\alpha]_D +60^\circ$ (c 0.7 CH₂Cl₂). The ³¹P {¹H}NMR spectrum of complex **169a** gave two doublet and one doublet of a doublet resonance signals at δ 35.8 (d, ³J_{PP} = 64.1Hz), 42.5 (d, ³J_{PP} = 24.4Hz) and 66.0 (dd, ³J_{pp} =

64.1 Hz, $J_{\text{PP}} = 24.4$ Hz). In solution the complex slowly transformed into its regioisomer **169b**, which showed one doublet of a doublet and two doublet resonance signals at δ 39.7 (d, $^3J_{\text{PP}} = 45.8$ Hz), 41.0 (dd, $^3J_{\text{PP}} = 45.8$ Hz, $J_{\text{PP}} = 21.0$ Hz) and 61.9 (d, $J_{\text{PP}} = 21.0$ Hz) in the $^{31}\text{P} \{^1\text{H}\}$ NMR spectrum. The equilibrium ratio was 3.4:1.

The molecular structure and absolute configuration of **169a** were subsequently confirmed by X-ray crystallography (Figure 4.5). Selected bond lengths and angles are given in Table 4.3. There are two crystallographically independent molecules in the asymmetric unit, which have identical stereochemistry and differ only slightly in bond lengths and angles. For clarity, only one molecule is given. The structural analysis affirmed that a five-membered diphosphine chelate adopting λ ring conformation was formed, and the newly formed stereogenic centre at P_1 (P_{1X} for the other molecule) was established to adopt the *S* absolute configuration. The geometry at palladium(II) is slightly distorted square plane with a distortion angle of 2.6° (2.0° for the other one) and a mean deviation from planarity of $0.017 \text{ \AA}$ ($0.025 \text{ \AA}$ for the other one). The P-Se distance is $2.108(3) \text{ \AA}$ [$2.096(4) \text{ \AA}$ for the other molecule], which is significantly longer than its P=S and P=O derivatives. The geometry at P_3 is distorted tetrahedral with angles in range of $104.9(5)^\circ$ to $114.0(2)^\circ$ [$104.4(4)^\circ \sim 113.3(2)^\circ$ for the other molecule]. As expected from the other derivatives, the phenyl ring at P_1 is locked to a position by the hydrogen at C_{14} , which is slightly above the plane of naphthyl ring protruding to the ring. These structural features are consistent with the observation of a multiplet resonance signal appeared at δ 6.83 in the ^1H NMR (CDCl_3) spectrum, indicating that the aromatic proton was indeed shielded by the phenyl ring. On the other hand, protons at C_{2A} and C_{6A} were deshielded by P_1 as a clear doublet of a doublet resonance signal exhibited downfield at δ 8.01.

Figure 4.5 Crystal Structure of Complex (*S,S*_p)-169a

Table 4.3 Selected Bond Lengths (Å) and Angles (deg) for Complex (S,Sp)-**169a**

Pd(1)-C(13)	2.06(1)	Pd(1)-N(1)	2.131(8)
Pd(1)-P(1)	2.236(3)	Pd(1)-P(2)	2.340(3)
Pd(2)-C(13X)	2.02(1)	Pd(2)-N(1X)	2.129(8)
Pd(2)-P(1X)	2.240(3)	Pd(2)-P(2X)	2.353(3)
Se(1)-P(3)	2.108(3)	P(1)-C(3)	1.81(1)
P(1)-C(1)	1.82(1)	P(1)-C(1A)	1.837(4)
P(2)-C(1C)	1.799(4)	P(2)-C(2)	1.82(1)
P(2)-C(1B)	1.827(4)	P(3)-C(4)	1.80(1)
P(3)-C(1E)	1.807(5)	P(3)-C(1D)	1.809(5)
P(1X)-C(3X)	1.80(1)	P(1X)-C(1F)	1.807(4)
P(1X)-C(1X)	1.85 (1)	P(2X)-C(1H)	1.792(4)
P(2X)-C(1C)	1.817(4)	P(2X)-C(2X)	1.86(1)
P(3X)-C(1J)	1.788(5)	P(3X)-C(1I)	1.821(5)
P(3X)-C(4X)	1.84(1)	P(3X)-Se(1X)	2.096(4)
C(13)-Pd(1)-N(1)	79.6(4)	C(13)-Pd(1)-P(1)	93.2(3)
N(1)-Pd(1)-P(1)	172.8(2)	C(13)-Pd(1)-P(2)	176.6(3)
N(1)-Pd(1)-P(2)	102.5(2)	P(1)-Pd(1)-P(2)	84.6(1)
C(13X)-Pd(2)-N(1X)	80.7(4)	C(13X)-Pd(2)-P(1X)	92.5(3)
N(1X)-Pd(2)-P(1X)	173.0(2)	C(13X)-Pd(2)-P(2X)	176.9(3)
N(1X)-Pd(2)-P(2X)	102.2(2)	P(1X)-Pd(2)-P(2X)	84.6(1)
C(3)-P(1)-C(1)	105.4(5)	C(3)-P(1)-C(1A)	107.6(4)
C(1)-P(1)-C(1A)	104.0(4)	C(3)-P(1)-Pd(1)	115.2(4)
C(1)-P(1)-Pd(1)	109.5(3)	C(1A)-P(1)-Pd(1)	114.2(2)
C(1C)-P(2)-C(2)	102.0(4)	C(1C)-P(2)-C(1B)	108.7(2)
C(2)-P(2)-C(1B)	107.0(4)	C(1C)-P(2)-Pd(1)	118.2(2)
C(2)-P(2)-Pd(1)	105.5(4)	C(1B)-P(2)-Pd(1)	114.3(2)
C(4)-P(3)-C(1E)	104.9(5)	C(4)-P(3)-C(1D)	105.4(4)
C(1E)-P(3)-C(1D)	106.7(2)	C(4)-P(3)-Se(1)	111.7(4)
C(1E)-P(3)-Se(1)	114.0(2)	C(1D)-P(3)-Se(1)	113.4(2)

4-2.3 Asymmetric Alkylation Reaction

When complex **164** was treated directly with excess MeI at room temperature in CH₂Cl₂ solvent, the alkylation reaction was found completed in one day. The ³¹P {¹H}NMR spectrum of the resulting mixture in CDCl₃ showed four sets of one doublet of a doublet and two doublet resonance signals at δ [24.6 (d, ³J_{PP} = 61.0Hz), 42.1 (d, J_{PP} = 22.9Hz) and 67.7 (dd, ³J_{pp} = 61.0Hz, J_{PP} = 22.9Hz)]; δ [26.1 (d, ³J_{pp} = 40.3Hz), 37.3 (dd, ³J_{PP} = 40.3Hz, J_{PP} = 21.1Hz) and 60.1 (d, J_{PP} = 21.1Hz)]; δ [26.4 (d, ³J_{PP} = 53.6 Hz), 42.9 (d, J_{PP} = 23.2 Hz) and 61.2 (dd, ³J_{PP} = 53.6 Hz, J_{PP} = 23.2 Hz)]; δ [26.2 (d, ³J_{PP} = 32.2 Hz), 36.8 (dd, ³J_{PP} = 32.2 Hz, J_{PP} = 22.0 Hz) and 60.1 (d, J_{PP} = 22.0 Hz)] in the ratio of 33.7:1:1:0.9. With the comparison of their oxide, sulfide and selenide analogues, these four sets of resonance signals were assigned to complexes **171a**, **171b**, **172a** and **172b**, respectively.

Scheme 4.2

The structure of isolated product was subsequently investigated by the X-ray crystallography. It was found to be two independent diastereomers (**171a** Figure 4.6 and **172a** Figure 4.7) in the asymmetric unit. The two isomers differed in the newly formed *P*-stereocentres. Selected bond lengths and angles are given in Table 4.4. The structural

analysis affirmed that a five-membered diphosphine chelate adopting λ ring conformation for **171a** and δ ring conformation for **172a** was formed. The newly formed stereogenic centre at P_5 is established to adopt the *Sp* absolute configuration in **171a**, and at P_2 is established to adopt the *Rp* absolute configuration in **172a**. Attempts to isolate complex **171a** or **172a** into its enantiomerically pure form were unsuccessful. Theoretically, upon removal of the chiral naphthylamine auxiliary from the mixture of complexes **171a** and **172a**, a mixture of racemic neutral dichloro palladium(II) complexes could be obtained. Similarly, the corresponding ligands liberated from the palladium(II) centres would also be racemic. Therefore, further study of this asymmetric alkylation reaction was not pursued.

Figure 4.6 Crystal Structure of Complex (*S,S*)-171a

Figure 4.7 Crystal Structure of Complex (*S,Rp*)-172a

Table 4.4 Selected Bond Lengths (Å) and Angles (deg) for Complexes (*S*,*Sp*)-**171a** and (*S*,*Rp*)-**172a**

Pd(1)-C(1)	2.071(7)	Pd(1)-N(1)	2.150(6)
Pd(1)-P(1)	2.375 (2)	Pd(1)-P(2)	2.253(2)
Pd(2)-C(50)	2.059(7)	Pd(2)-N(2)	2.150(6)
Pd(2)-P(5)	2.248(2)	Pd(2)-P(4)	2.354(2)
P(1)-C(27)	1.830(8)	P(2)-C(28)	1.866(7)
P(2)-C(35)	1.853(7)	P(3)-C(36)	1.810(7)
P(3)-C(49)	1.794(7)	P(5)-C(77)	1.833(7)
P(4)-C(76)	1.815(7)	P(5)-C(84)	1.823(7)
P(6)-C(85)	1.804(7)	P(6)-C(98)	1.779(9)
C(1)-Pd(1)-N(1)	79.5(2)	C(1)-Pd(1)-P(2)	93.7(2)
N(1)-Pd(1)-P(2)	173.1(2)	C(1)-Pd(1)-P(1)	177.9(2)
N(1)-Pd(1)-P(1)	102.4(2)	P(2)-Pd(1)-P(1)	84.4(1)
C(50)-Pd(2)-N(2)	80.0(3)	C(50)-Pd(2)-P(5)	94.7(2)
P(5)-Pd(2)-N(2)	170.1(2)	C(50)-Pd(2)-P(4)	175.2(2)
P(4)-Pd(2)-N(2)	101.8(2)	P(5)-Pd(2)-P(4)	84.2(1)
C(37)-P(3)-C(43)	110.2(3)	C(37)-P(3)-C(49)	110.5(4)
C(43)-P(3)-C(49)	109.5(4)	C(37)-P(3)-C(36)	108.4(3)
C(43)-P(3)-C(36)	107.5(3)	C(49)-P(3)-C(36)	110.6(3)
C(98)-P(6)-C(85)	108.6(4)	C(98)-P(6)-C(92)	108.6(4)
C(85)-P(6)-C(92)	107.7(3)	C(98)-P(6)-C(86)	112.1(4)
C(85)-P(6)-C(86)	106.8(4)	C(92)-P(6)-C(86)	112.9(3)

4-2.4 Removal of Chiral Auxiliary from (*S*,*Sp*)-**165a**, (*S*,*Sp*)-**167a**, (*S*,*Sp*)-**169a** to Generate (*Sp*)-**173**, (*Sp*)-**174** and (*Sp*)-**175**

Complex (*Sp*)-**173** was obtained (Scheme 4.3) from the chemoselective removal of naphthylamine auxiliary from complex **165a**. The dichloro complex was obtained as white crystals in 89% yield, mp 306-308 °C (decomp.), $[\alpha]_D +23^\circ$ (*c* 0.3 CH₂Cl₂). The ³¹P

$\{^1\text{H}\}$ NMR spectrum (in CDCl_3) of the pure complex (Sp)-**173** in CDCl_3 exhibited two doublet and one doublet of a doublet resonance signals at δ 33.2, 65.1 and 75.5.

Scheme 4.3

Similarly complex (Sp)-**174** was generated (Scheme 4.3) after removal of naphthyl amine auxiliary from complex **167a** and purified by crystallization as light yellow crystals in 60% yield, mp 295-297 °C (decomp.), $[\alpha]_{\text{D}} +28^\circ$ (c 0.2 CH_2Cl_2). At room temperature, the ^{31}P $\{^1\text{H}\}$ NMR spectrum of complex (Sp)-**174** in CDCl_3 showed three broad peaks (Figure 4.8) with the similar intensities. As temperature was increased to 328K, two peaks at δ 66.9 and 67.8 (300K) were merged into one broad signal at δ 67.5 (328K) leaving the intensity of the signal at δ 44.1 (300K) unchanged. While at a lower temperature (253K), a set of one triplet and two doublet of doublet resonance signals displaced at δ 43.8 (t, $J_{\text{PP}} = J_{\text{PP}} = 7.6\text{Hz}$), 66.5 (dd, $J_{\text{PP}} = 7.6\text{Hz}$, $J_{\text{PP}} = 19.1\text{Hz}$) and 68.2 (dd, $J_{\text{PP}} = 7.6\text{Hz}$, $J_{\text{PP}} = 19.1\text{Hz}$). All these spectra are reversible by adjusting the temperature of the NMR spectrometer. Clearly this is a temperature dependent dynamic process occurring when complex (Sp)-**174** is dissolved in solution. A hypothesis of this process will be discussed later.

Figure 4.8 VT ^{31}P $\{^1\text{H}\}$ NMR Spectrum of Complex (Sp)-**174** in CDCl_3

In solid state, complex (Sp)-**174** was crystallized as shown in Figure 4.9. Selected bond lengths and angles are given in Table 4.5. The geometry at palladium(II) is retained as slightly distorted square plane with a distortion angle of 6.8° and a mean deviation from planarity of $0.092 \text{ \AA}$. The intraligand angles at the palladium(II) atom are $\text{P}_1\text{-Pd-P}_2$ $85.5(1)^\circ$ and $\text{Cl}_1\text{-Pd-Cl}_2$ $95.5(1)^\circ$ and the interligand angles are $\text{Cl}_2\text{-Pd-P}_2$ $90.6(1)^\circ$ and $\text{Cl}_1\text{-Pd-P}_1$ $88.7(1)^\circ$. The structural analysis affirmed that a five-membered diphosphine chelate adopting λ ring conformation was formed, and the stereogenic centre at P_1 was established to retain as *S* absolute configuration. The P-S bond distance at P_3 is $1.959(1) \text{ \AA}$. This is consistent with a P=S double bond, although it is slightly longer than its counterpart in complex **167a** [$1.948(2) \text{ \AA}$].

Figure 4.9 Crystal Structure of Complex (Sp)-174

Table 4.5 Selected Bond Lengths (Å) and Angles (deg) for Complex (Sp)-**174**

Pd(1)-Cl(1)	2.374(1)	Pd(1)-Cl(2)	2.360(1)
C(15)-P(1)	1.816(2)	P(1)-C(21)	1.825(2)
P(1)-C(14)	1.828(3)	P(1)-Pd(1)	2.226(1)
P(2)-C(1)	1.799(2)	P(2)-C(7)	1.816(2)
P(2)-C(13)	1.831(2)	P(2)-Pd(1)	2.236(1)
P(3)-C(29)	1.805(3)	P(3)-C(23)	1.812(3)
P(3)-C(22)	1.822(2)	P(3)-S(1)	1.96(1)
C(15)-P(1)-C(21)	106.1(1)	C(15)-P(1)-C(14)	106.2(1)
C(21)-P(1)-C(14)	105.3(1)	C(15)-P(1)-Pd(1)	111.8(1)
C(21)-P(1)-Pd(1)	117.3(9)	C(14)-P(1)-Pd(1)	109.5(1)
C(1)-P(2)-C(7)	108.1(1)	C(1)-P(2)-C(13)	106.5(1)
C(7)-P(2)-C(13)	105.2(1)	C(1)-P(2)-Pd(1)	117.8(1)
C(7)-P(2)-Pd(1)	109.5(8)	C(13)-P(2)-Pd(1)	109.0(1)
C(29)-P(3)-C(23)	107.2(1)	C(29)-P(3)-C(22)	108.1(1)
C(23)-P(3)-C(22)	103.7(1)	C(29)-P(3)-S(1)	112.3(1)
C(23)-P(3)-S(1)	112.7(1)	C(22)-P(3)-S(1)	112.4(1)
P(1)-Pd(1)-P(2)	85.5(1)	P(1)-Pd(1)-Cl(2)	174.6(1)
P(2)-Pd(1)-Cl(2)	90.6(1)	P(1)-Pd(1)-Cl(1)	88.7(1)
P(2)-Pd(1)-Cl(1)	171.6(1)	Cl(2)-Pd(1)-Cl(1)	95.5(1)

Complex (Sp)-**175** was generated (Scheme 4.3) after removal of naphthyl auxiliary from complex **169a** and purified by crystallization as light yellow crystals in 90% yield, mp 232-233 °C (decomp.), $[\alpha]_D +32^\circ$ (c 0.2 CH₂Cl₂). At room temperature the ³¹P {¹H}NMR (CDCl₃) spectrum of complex (Sp)-**175** showed two broad peaks at δ 30.8 and 66.5.

In solid state, complex (Sp)-**175** crystallized as an ionic complex with perchlorate as counter ion (Figure 4.10). Selected bond lengths and angles are given in Table 4.6. Both five-membered ring adopting λ conformation and six-membered ring adopting chair conformation are formed at palladium(II) centre. The stereogenic centre at P_2 is established

to retain *Sp* absolute configuration. The geometry at palladium(II) is retained as distorted square plane with a distortion angle of 5.2° and a mean deviation from planarity of $0.064 \text{ \AA}$. The intraligand angles at the palladium(II) atom are $\text{P}_2\text{-Pd-P}_2$ $85.4(1)^\circ$ and $\text{Cl}_1\text{-Pd-Se}$ $90.3(1)^\circ$ and the interligand angles are Se-Pd-P_2 $91.55(2)^\circ$ and $\text{Cl}_1\text{-Pd-P}_3$ $92.9(1)^\circ$. In this molecule the selenium atom attaches to palladium(II) by replacing a Cl atom with a distance of Pd-Se as $2.502(1) \text{ \AA}$. The distance of Pd-Se is significantly longer than the distance of Pd-Cl₁ $2.339(1) \text{ \AA}$. The Pd-P₂ $2.232(1) \text{ \AA}$ and Pd-P₃ $2.266(1) \text{ \AA}$ bond distances are significantly shorter than their counterparts in their precursor complex **169a**. This observation is consistent with the weaker *trans* influences of the chloro and Se ligands in complex (*S*)-**175**, when compared to the strong influences of the C and N atoms in complex **169a**. It should be noted that (*S*)-**175** is a stable molecule with the optical rotation value $[\alpha]_{\text{D}} +122^\circ$ (*c* $0.6 \text{ CH}_2\text{ClCH}_2\text{Cl}$), which remained unchanged even after being stored for two weeks.

As previously described, VT NMR spectroscopy detected that complex (*Sp*)-**174** showed fluxional behavior in solution monitored by. It is hypothesized that the sulfur atom can replace the chlorine atom, which is *cis* to the chiral phosphorus atom. The long arm $[-\text{C}_2\text{H}_4\text{P}(\text{S})\text{Ph}_2]$ substituent at the chiral phosphorus atom enables the sulfur atom to attach to palladium(II) centre in terms of stereochemistry. In addition, as an evidence, the X-ray crystallography of complex (*Sp*)-**175** affirms that the selenium atom is bonding to palladium(II) centre by replacing the chlorine atom, which is *cis* to the chiral phosphorus atom. Therefore, in complex (*Sp*)-**174**, which is the analogue of complex (*Sp*)-**175**, the sulfur atom can also attach to palladium(II) centre. Apparently, the displacement process is more active in higher temperature while hindered in lower temperature. Additionally, the P=S bond is stronger and shorter than the P=Se bond, thus the crystallized complex (*Sp*)-**174** is a dichloro complex, as expected.

Figure 4.10 Crystal Structure of Complex (Sp)-175

Table 4.6 Selected Bond Lengths (Å) and Angles (deg) for Complex (Sp)-**175**

Pd(1)-P(2)	2.232(1)	Pd(1)-P(3)	2.266(1)
Pd(1)-Cl(1)	2.340(1)	Pd(1)-Se(1)	2.502(1)
P(1)-Se(1)	2.153(1)	P(1)-C(1)	1.821(3)
P(2)-C(2)	1.817(3)	P(2)-C(3)	1.842(3)
P(3)-C(4)	1.836(3)	C(1)-C(2)	1.524(4)
C(3)-C(4)	1.516(5)	P(2)-Pd(1)-P(3)	85.4(1)
P(2)-Pd(1)-Cl(1)	177.8(1)	P(3)-Pd(1)-Cl(1)	92.9(1)
P(2)-Pd(1)-Se(1)	91.6(2)	P(3)-Pd(1)-Se(1)	174.1(1)
Cl(1)-Pd(1)-Se(1)	90.3(1)	P(1)-Se(1)-Pd(1)	98.1(1)
C(23)-P(1)-C(29)	110.4(1)	C(23)-P(1)-C(1)	108.2(1)
C(1)-P(1)-C(29)	105.1(1)	C(23)-P(1)-Se(1)	112.1(1)
Se(1)-P(1)-C(29)	109.3(1)	C(1)-P(1)-Se(1)	111.6(1)
C(17)-P(2)-C(2)	109.0(1)	C(17)-P(2)-C(3)	105(1)
C(3)-P(2)-C(2)	103.3(2)	C(17)-P(2)-Pd(1)	113.4(1)
Pd(1)-P(2)-C(2)	116.3(1)	Pd(1)-P(2)-C(3)	108.9(1)
C(11)-P(3)-C(5)	106.2(1)	C(11)-P(3)-C(4)	108.5(1)
C(4)-P(3)-C(5)	103.7(2)	C(11)-P(3)-Pd(1)	118.0(1)
C(5)-P(3)-Pd(1)	112.6(1)	C(4)-P(3)-Pd(1)	106.9(1)
C(2)-C(1)-P(1)	115.4(2)	C(1)-C(2)-P(2)	117.6(2)
C(4)-C(3)-P(2)	107.6(2)	C(3)-C(4)-P(3)	107.7(2)

4-2.5 Liberation of Free Ligand (Sp)-**176**

Free *P*-chiral phosphine mono-oxide compound (Sp)-**176** was liberated (Scheme 4.4) from complex (Sp)-**173** with treatment of aqueous KCN and isolated as stable white solid in 90% yield, mp 177-179 °C, $[\alpha]_D$ -16° (c 0.3 CH₂Cl₂). Pure (Sp)-**176** gave two doublet and one doublet of a doublet phosphorus resonance signals at δ -16.2 (dd, $^3J_{PP}$ = 42.0 Hz, J_{PP} = 30.5 Hz), -12.8 (d, J_{PP} = 30.5 Hz) and 32.5 (d, $^3J_{PP}$ = 42.0 Hz). As expected, compound (Sp)-**176** can be oxidized by H₂O₂ to form the achiral trioxide compound **178**,

which showed one doublet resonance signal at δ 33.9 and one triplet resonance signal at δ 43.1 with a phosphorus-phosphorus coupling constant of 50.4 Hz in ^{31}P $\{^1\text{H}\}$ NMR spectrum (in CDCl_3). In order to verify the enantiomeric purity of compound (Sp)-**176**, the method of re-complexation to *S*- and *R*-form naphthylamine auxiliary palladium(II) complexes was carried out (Scheme 4.4). As expected, re-complexation of (S)-**176** and (S)-**60** gave complexes **165a** and **165b**. The ^{31}P $\{^1\text{H}\}$ NMR spectrum of the mixture of product in CDCl_3 showed a set of two doublet and one doublet of a doublet resonance signals at δ 31.0, 42.0 and 67.3; together with a set of two doublet and one doublet of a doublet phosphorus resonance signals at δ 33.0, 43.3 and 62.3 in an equilibrium ratio of 1:1. Similarly the re-complexation of (Sp)-**176** and (R)-**60** gave complexes **177a** and **177b** which are enantiomers of **166a** and **166b** respectively. The ^{31}P $\{^1\text{H}\}$ NMR spectrum of the re-complexation product mixture in CDCl_3 showed a set of two doublet and one doublet of a doublet resonance signals at δ 33.6, 42.2 and 60.8; together with a set of two doublet and one doublet of a doublet phosphorus resonance signals at δ 32.4, 43.5 and 61.6 in an equilibrium ratio of 1:4, respectively. Importantly, since the phosphorus resonance signals at δ (31.0, 42.0 and 67.3) and (33.0, 43.3 and 62.3) were not observed. The absence of these signals confirmed the optical purity of the liberated phosphine mono-oxide ligand (Sp)-**176** [also complex (Sp)-**173**]. From these recoordination experiments, spectroscopic and crystallographic studies, the four stereoisomeric products generated in the oxidation reaction of complex **164** have been established to be complexes **165a**, **b** and **166a**, **b** unambiguously.

Scheme 4.4

It should be noted that the phosphorus-phosphorus coupling constants have changed after the removal of naphthyl auxiliary and the liberation of free phosphine mono-oxide. It has been established¹²⁴ that the phosphorus-phosphorus coupling within a chelate ring can be factored into “through-the-backbone” ($^B J_{PP}$) and “through-the-metal” ($^M J_{PP}$) contributions, where $^B J_{PP}$ is assumed to be equal to that in the free ligand. It has been also reported that in five-membered chelate rings, the magnitudes of $^B J_{PP}$ and $^M J_{PP}$ are nearly equal but of opposite sign, which leads to a smaller observed J_{PP} value. The J_{PP} of the two chelate phosphorus units was 26.7 Hz in complex **165a** which is almost the same as that of free phosphine mono-oxide **176** (30.5 Hz); but decreased to near zero (9.2 Hz) in the dichloro complex **173**. It was possible that the nitrogen atom and naphthyl ring affected the $^M J_{PP}$ value as well as the unsymmetrical chelated ligand so that $^B J_{PP}$ and $^M J_{PP}$ did not exactly cancel each other. On the other hand, coupling between phosphine oxide and one of the coordinated phosphorus atom must be transmitted via the carbon backbone since they were not both located in the chelated ring¹²⁵. There were no coupling constants observed for the two terminal phosphorus units (in ligand **163**) in both complexes of **165a** and **173**, neither in ligand **176**. However the coupling constant of the uncoordinated phosphorus unit

and the centre phosphorus unit (in ligand **163**) was 61.0Hz in complex **165a** which was almost the same as that in complex **173** (58.0Hz); but decreased to 42.0Hz in ligand **176**.

4-2.6 Removal of Palladium Centre from Complexes (Sp)-**174** and (Sp)-**175**

The corresponding tridentate phosphine mono-sulfide ligand and mono-selenide ligand were attempted to be liberated from their palladium(II) precursors (Sp)-**174** and (Sp)-**175**, respectively. It was found surprisingly that the resulting ligands did not show any optical activities, as their optical rotation values were always zero even though it was measured in different solvents or in different wavelength. It should be noted that the liberated ligands were generated from enantiomerically pure complexes [(Sp)-**174** and (Sp)-**175**]. Moreover, the liberation was followed by an established method. Additionally there were no other chiral materials introduced, indicating that the chirality of the corresponding ligands could not be destroyed by the reagent used during the liberation process. Therefore, there should be some transformation of sulfur and selenium atoms between two phosphorus units occurred, after the ligands came off from the palladium(II) stabilization.

Dating back to 1930s, the transfer of sulfur atom from P(V) to P(III) was firstly discovered¹²⁶. Numerous synthetic applications were developed based on the transfer process, either for the purpose of preparation of P(III) ligands¹²⁷ (Fig. 4.1 eq. 1) or P(V) ligands¹²⁸ (Fig. 4.1 eq. 2). Later on, it was found that the transfer process not only took place between two molecules containing P(III) and P(V), but also occurred within a molecule containing both P(III) and P(V) atoms¹²⁹ (Fig. 4.1 eq. 3). Kinetic studies indicated that the transfer process involved a transition state in which sulfur atom attached to both phosphorus units¹³⁰. Similarly the transfer of selenium from tertiary phosphine selenides to tertiary phosphines appeared generally. The transformation reaction was found fast on NMR time scale¹³¹. The isomerization of the liberated ligands **179** and **180** from complexes

(Sp)-**174** and (Sp)-**175** was explained in Scheme 4.5. Upon removal of the palladium(II) stabilization, sulfur and selenium atoms could bond to either of the two terminal P(III) atoms, therefore the chiral phosphorus units racemized rapidly. Thus no optical activities could be detected from the liberated ligands **179** and **180** from complexes (Sp)-**174** and (Sp)-**175**, respectively.

Fig. 4.1

Scheme 4.5

4-3 Conclusion

Chiral palladium(II) template can be used for synthesis of chiral diphosphine ligands functionalized by phosphorus chalcogen group by controlling the stereo- and regio-selectivity. It is suitable for creating a phosphorus chiral centre at a non-chiral triphosphine ligand by selectively oxidizing one P(III) atom to P(V) atom. It is also confirmed that P=O bond is much more stable than P=S or P=Se, and experimentally proved that without palladium(II) stabilization the ligands liberated from complexes (Sp)-**174** and (Sp)-**175** are racemic. In addition, it has been demonstrated that P-C bond could be formed by direct reacting of P(III) with MeI.

4-4 Experimental Section

Attempted synthesis of complexes **165**, **166** followed by isolation of [SP-4-4-{(S)-1-[1-(dimethylamino)ethyl]naphthyl- C^2,N } {(S)-1-diphenylphosphino-2-(2'-diphenyloxophosphinoethyl)-phenylphosphino-ethane- P^1,P^2 }] palladium(II) perchlorate, (S, S_P)-**165a**. Complex (S)-**60** (1.029g, 2.1mmol) and triphosphine **163** (1.131g, 2.1mmol) were dissolved in dichloromethane (50 mL) and the mixture stirred for 1 hour. VT ^{31}P { 1H }NMR spectrum was observed immediately.

To the mixture solution, 10 ml of 30 % H_2O_2 was added under vigorous stirring for 1 hour. The mixture was subsequently washed with water (3 x 30 mL) and dried with $MgSO_4$. (S, S_P)-**165a** was crystallized dichloromethane and ether as colourless crystals: mp 205-206 °C (decomp.); $[\alpha]_D +79^\circ$ (c 0.3g CH_2Cl_2); 1.253g (62% yield). Anal. Calcd for $C_{48}H_{49}P_3ClO_5PdN$: C, 60.4; H, 5.2; N, 1.5. Found C, 60.0; H, 4.8; N, 1.8. ^{31}P { 1H }NMR ($CDCl_3$) δ 67.3 (dd, 1P, $^3J_{pp} = 61.0Hz$, $J_{PP} = 26.7Hz$, P), 41.9 (d, 1P, $J_{PP} = 26.7Hz$, P), 31.0 (d, 1P, $^3J_{PP} = 61.0Hz$, P); 1H NMR δ 2.05 (d, 3H, $^3J_{HH} = 6.5Hz$, CHMe), 2.58 (d, 3H, $^4J_{PH} = 1.2Hz$, NMeax), 2.68 (dd, 3H, $^4J_{PH} = 3.6Hz$, $^4J_{PH} = 3.3Hz$, NMeeq); 1.84-2.83 (m, 8H, 4CH₂); 4.64 (dq, 1H, $^2J_{HH} = ^4J_{PH} = 6.5Hz$, CHMe); 6.82 (ddd, 1H, $J_{PH} = 4.8Hz$, $J_{PH} = 6.7Hz$, $^3J_{HH} = 8.3Hz$, PdCCH); 6.88-7.89 (m, 28H, aromatics); 8.02 (ddd, 2H, $J_{PH} = 7.5Hz$, $^3J_{HH} = 6.9Hz$, $^4J_{HH} = 1.5Hz$, 2PCH).

Removal of naphthylamine auxiliary for synthesis of [SP-4-3-(S)-dichloro{(S)-1-diphenylphosphino-2-(2'-diphenyloxophosphinoethyl)-phenylphosphino-ethane- P^1,P^2 }]palladium(II), (Sp)-173 and liberation of (S)- 2-diphenylphosphino-1-(2'-diphenylphosphinylethyl)-phenylphosphino-ethane, (Sp)-176. To the solution of complex (S, S_P)-**165a** (0.561g, 0.6mmol) in dichloromethane, 15ml of conc. hydrochloric acid was added. After vigorous stirring overnight, the mixture was extracted with water (3 x 30 mL) and dried with $MgSO_4$. Complex (Sp)-**173** was crystallized in dichloromethane and diethyl ether as yellow crystals: mp 306-308 °C (decomp.); $[\alpha]_D +23^\circ$ (c 0.30 CH_2Cl_2);

0.381g (89% yield). Anal. Calcd for $C_{34}H_{33}P_3Cl_2O$ Pd: C, 56.1; H, 4.6; Found C, 56.2; H, 4.6. $^{31}P \{^1H\}$ NMR ($CDCl_3$) δ 33.2 (d, 1P, $^3J_{PP} = 58.0$ Hz, P), 65.1 (d, 1P, $J_{PP} = 9.2$ Hz, P), 75.5 (dd, 1P, $^3J_{PP} = 58.0$ Hz, $J_{PP} = 9.2$ Hz, P); 1H NMR ($CDCl_3$) δ 2.00-2.75 (m, 8H, $4CH_2$); 7.38-8.04 (m, 25H, aromatics).

A solution of complex (Sp)-**173** (0.040g, 0.05mmol) in dichloromethane (30mL) was stirred vigorously with a saturated aqueous solution of potassium cyanide (1g) for 1 hour. The resulting colourless organic layer was separated, washed with water, and dried with $MgSO_4$. White solid (Sp)-**176** was isolated from dichloromethane and diethyl ether: mp 177-179 °C; $[\alpha]_D -16^\circ$ (c 0.3g CH_2Cl_2); 0.027g (90% yield). Anal. Calcd for $C_{34}H_{33}P_3O$: C, 74.2; H, 6.0; Found C, 73.8; H, 6.0. $^{31}P \{^1H\}$ NMR ($CDCl_3$) δ -16.2 (dd, 1P, $J_{PP} = 30.5$ Hz, $^3J_{PP} = 42.0$ Hz, P), -12.8 (d, 1P, $^3J_{PP} = 30.5$ Hz, P), 32.5 (d, 1P, $^3J_{PP} = 42.0$ Hz, P); 1H NMR ($CDCl_3$) δ 1.63-2.25 (m, 8H, $4CH_2$); 7.26-7.27 (m, 25H, aromatics).

Attempted synthesis of complexes 167, 168 and isolation of [SP-4-4-((S)-1-[1-(dimethylamino)ethyl]naphthyl- C^2,N) {(S)-1-diphenylphosphino-2-(2'-diphenyloxophosphinoethyl)-phenylphosphino-ethane- P^1,P^2 }] palladium(II) perchlorate, (S, S_P)-167a**.** To the mixture of complex (S)-**60** (1.216g, 2.5mmol) and triphosphine **163** (1.336g, 2.5mmol), 0.08g elemental sulfur was added for vigorous stirring overnight. After purification by column chromatography, complex (S, S_P)-**167a** was isolated as colourless crystals via crystallization in dichloromethane and diethyl ether: mp 197-198 °C (decomp.); $[\alpha]_D +79^\circ$ (c 0.4g CH_2Cl_2); 1.34g (55% yield). Anal. Calcd for $C_{48}H_{49}P_3ClS O_4Pd N$: C, 59.4; H, 5.1; N, 1.4. Found C, 60.0; H, 4.8; N, 1.8. $^{31}P \{^1H\}$ NMR ($CDCl_3$) δ 42.4 (d, 1P, $J_{PP} = 24.4$ Hz, P), 43.2 (d, 1P, $^3J_{PP} = 61.0$ Hz, P), 66.6 (dd, 1P, $^3J_{PP} = 61.0$ Hz, $J_{PP} = 24.4$ Hz, P); 1H NMR ($CDCl_3$) δ 2.05 (d, 3H, $^3J_{HH} = 6.5$ Hz, $CHMe$), 2.58 (d, 3H, $^4J_{PH} = 1.2$ Hz, NMe_{ax}), 2.68 (dd, 3H, $^4J_{PH} = 3.7$ Hz, $^4J_{PH} = 3.2$ Hz, NMe_{eq}); 1.83-3.04 (m, 8H, $4CH_2$); 4.63 (dq, 1H, $^2J_{HH} = ^4J_{PH} = 6.5$ Hz, $CHMe$); 6.86 (m, 1H, $PdCCH$); 7.14-8.00 (m, 28H, aromatics); 8.03 (dd, 2H, $J_{PH} = 12.0$ Hz, $^3J_{HH} = 7.0$ Hz, $2PCH_2$).

Removal of naphthylamine auxiliary for synthesis of [SP-4-3-(S)-Dichloro{(S)-1-diphenylphosphino-2-(2'-diphenyloxophosphinoethyl)-phenylphosphino-ethane- P^1 , P^2 }] palladium(II), (Sp)-174. To the solution of complex (S, S_P)-**167a** (0.741g, 1.0mmol) in dichloromethane, 15ml of conc. hydrochloric acid was added. After vigorous stirring overnight, the mixture was extracted with water (3 x 30) and dried with MgSO₄. Complex (Sp)-**174** was crystallized in dichloromethane and diethyl ether as yellow crystals: mp 295-297 °C (decomp.); [α]_D +28° (*c* 0.20 CH₂Cl₂); 0.341g (60% yield). Anal. Calcd for C₃₄H₃₃P₃Cl₂S Pd: C, 54.9; H, 4.5. Found C, 54.5; H, 4.2. ³¹P {¹H}NMR (DMSO-*d*₆) δ 45.2 (d, 1P, J_{PP} = 19.3Hz, J_{PP} = 8.8Hz, P), 70.8 (d, 1P, J_{PP} = 19.1Hz, J_{PP} = 8.8Hz, P), 71.3 (dd, 1P, J_{PP} = 19.1Hz, J_{PP} = 19.3Hz, P); ¹H NMR (DMSO-*d*₆) δ 2.10-3.21 (m, 8H, 4CH₂); 7.51-8.40 (m, 25H, aromatics).

Attempted synthesis of complexes 169, 170 and isolation of complex [SP-4-4-{(S)-1-[1-(dimethylamino)ethyl]naphthyl- C^2 , N }{(S)-1-diphenylphosphino-2-(2'-diphenylsulfophosphinoethyl)-phenylphosphino-ethane- P^1 , P^2 }] palladium(II) perchlorate, (S, S_P)-169a. To the mixture of complex (S)-**60** (1.216g, 2.5mmol) and triphosphine **163** (1.336g, 2.5mmol), 0.4g elemental selenium was added under vigorous stirring overnight. After filtration of excess selenium solid, the solution was concentrated and colourless crystals (S, S_P)-**169a** were separated upon adding diethyl ether: mp 217-218 °C (decomp.); [α]_D +60° (*c* 0.7g CH₂Cl₂); 2.290g (90% yield). Anal. Calcd for C₄₈H₄₉P₃ClO₄Pd N Se: C, 56.7; H, 4.9; N, 1.4. Found C, 56.3; H, 4.6; N, 1.5. ³¹P {¹H}NMR (CDCl₃) δ 35.8 (d, 1P, $^3J_{PP}$ = 64.1Hz, P), 42.5 (d, 1P, J_{PP} = 24.4Hz, P), 66.0 (dd, 1P, $^3J_{PP}$ = 64.1Hz, J_{PP} = 24.4Hz, P); ¹H NMR (CDCl₃) δ 2.04 (d, 3H, $^3J_{HH}$ = 6.5Hz, CHMe), 2.56 (s, 3H, NMeax), 2.66 (dd, 3H, $^4J_{PH}$ = 2.5Hz, $^4J_{PH}$ = 3.1Hz, NMeeq); 1.78-3.80 (m, 8H, 4CH₂); 4.63 (dq, 1H, $^2J_{HH}$ = $^4J_{PH}$ = 6.5Hz, CHMe); 6.83 (m, 1H, PdCCH); 7.60-7.86 (m, 28H, aromatics); 8.01 (dd, 2H, J_{PH} = 7.4Hz, $^3J_{HH}$ = 7.0Hz, 2PCH).

Removal of naphthylamine auxiliary for synthesis of [SP-4-3-{(S)-chloro-{(S)-1-diphenylphosphino-2-(2'-diphenylselenophosphinoethyl)-phenylphosphino-ethane-Se,P¹,P²}] palladium(II), (Sp)-175. To the solution of complex (S,Sp)-169a (1.002g, 1.2mmol) in dichloromethane, 15ml of conc. hydrochloric acid was added. After vigorous stirring overnight, the mixture was extracted with water (3 x 30 mL) and dried with MgSO₄. Complex (Sp)-175 was crystallized in dichloromethane and diethyl ether as yellow crystals: mp 232-233 °C (decomp.); [α]_D +32° (c 0.20 CH₂Cl₂); 0.421g (50% yield). Anal. Calcd for C₃₄H₃₃P₃Cl₂SePdO₄: C, 47.8; H, 3.9. Found C, 48.1; H, 3.8. ³¹P{¹H}NMR (DMSO-d₆) δ 31.0 (dd, 1P, J_{PP} = 20.5Hz, J_{PP} = 9.4Hz, P), 69.1 (dd, 1P, J_{PP} = 9.0Hz, J_{PP} = 9.4Hz, P), 70.2 (dd, 1P, J_{PP} = 9.0Hz, J_{PP} = 20.5Hz, P); ¹H NMR (DMSO-d₆) δ 2.21-3.50 (m, 8H, 4CH₂); 7.54-8.27 (m, 25H, aromatics).

Attempted synthesis of complexes [SP-4-3-{(S)-1-[1-(dimethylamino)ethyl]naphthyl-C²,N} {(S)or (R)-1-diphenylphosphino-2-(2'-diphenyl-methyl-phosphoranyl-ethyl)-phenylphosphino-ethane-P¹,P²}] palladium(II) 2 hexafluorophosphate, 171a and 172a . To the mixture of complex (S)-60 (1.302g, 2.7mmol) and triphosphine 163 (1.425g, 2.7mmol), 0.5 mL MeI solution was added under vigorous stirring overnight. The solvent of dichloromethane was removed followed by adding 30 mL of methanol as solvent. 10 equiv. of NH₄PF₆ was dissolved in 30 mL distilled water and added into the methanol mixture. The diastereomeric products 171 and 172 were obtained as white precipitate, which could be separated from the methanol-water solution. The isolated white precipitate was redissolved in dichloromethane followed by adding diethyl ether. Complexes (S,Sp)-171a, (S,R_P)-172a were co-crystallized as colourless prism, 0.153g (5% yield).

Typical procedure used for the re-complexation reactions. Stoichiometric amounts of complex (S)-60 or (R)-60 and free ligand (Sp)-176 were stirred in dichloromethane separately at room temperature and the solution was monitored by ³¹P

$\{^1\text{H}\}$ NMR spectroscopy until equilibrium was established.

Crystal Structure Determination. Complexes **(S,S_P)-165a**, **(S,S_P)-167a** and **(S,S_P)-169a** were analyzed at the National University of Singapore.

Complexes **(S,S_P)-171a**, **(S,R_P)-172a**, **(S_P)-174** and **(S_P)-175** were analyzed at Nanyang Technological University.

CHAPTER

5

CHIRAL PALLADIUM TEMPLATE INDUCED ASYMMETRIC HYDROPHOSPHINATION REACTION

5-1 Introduction

Functionalities play a significant role in classical organic chemistry, as in certain cases they can determine the fundamental physical and chemical properties of the organic molecules that they are attached to⁸⁷. Therefore introducing particular functional groups into enantiomerically pure phosphine ligands may enhance their reactivity as efficient catalysts in asymmetric synthesis. Indeed optically active phosphine ligands containing selected functionalities have been extensively used in asymmetric organic synthesis, biochemistry and chemotherapy^{88, 92}. It has been demonstrated that these activities and selectivities are controlled successfully by selected functionalities and their stereochemistry within a particular chiral phosphine supporter⁸³. For example, ligands containing phosphorus units and amides or amines or esters or hydroxy groups can dramatically improve both the stereoselectivity and the reactivity of these stereochemically demanding catalytic processes⁸⁴⁻¹⁰⁰. Despite their important roles in many aspects of science, the synthesis of these reactive and potentially unstable chiral ligands remains a major challenge. In this chapter, the chiral organopalladium complex promoting

hydrophosphonation reaction has been applied to the asymmetric synthesis of functionalized phosphine ligands.

Addition of phosphorus-hydrogen bonds to unsaturated carbon-carbon bonds can proceed by thermal¹³², acidic¹³³, basic¹³⁴, or free radical¹³⁵ pathways; or can be catalyzed¹³⁶ by transition metals such as palladium, platinum, nickel, rhodium or their complexes. Asymmetric addition of P-H moiety to unsaturated C-C bonds activated by metal complexes has been reported for synthesizing of chiral monophosphines¹³⁷. It has been reported that a chiral palladium(II) template has promoted reaction between diphenylphosphine and (*E*)- or (*Z*)-diphenyl-1-propenylphosphine successfully both in regio- and stereo-selectivities (Scheme 1.82)¹⁰³. The diphenylphosphino groups were added to the β -carbon of the vinylphosphines to form five-membered chelate rings exclusively. In this chapter, a bulky phenyl substituted diphenylvinylphosphine was reacted with diphenylphosphine in the presence of the chiral palladium template (*S*)-**60**. The use of a phenyl substituent is to verify whether the regio- and stereo-selectivity of the reaction could be improved.

The synthesis of vinylic phosphine ligands would generally produce a mixture of *cis*- and *trans*-isomers. These isomers cannot easily be separated into their isomerically pure form. On the other hand, adding of 2 equiv. of secondary phosphine ligands to C-C triple bonds within an organic unsaturated compound would generate bidentate phosphine ligands directly in only one single step thus avoiding the separation of intermediate *cis*- and *trans*-vinylic phosphine isomers. Theoretically, the introduction of a chiral palladium template and the steric configuration within the bidentate phosphine ligands may promote the hydrophosphination reaction of secondary phosphine ligands and organic triple bond compounds to proceed smoothly and selectively. In this chapter, diphenylphosphine was used for addition to an unsaturated triple bond. Two electron withdrawing ester substituted

acetylene, DMAD, was used as the starting material for the addition reaction and the chiral palladium(II) template (*S*)-**60** was used as reaction promoter.

5-2 Results and Discussion

5-2.1 Hydrophosphination Reaction between Diphenyl(styryl)phosphine and Diphenylphosphine

The hydrophosphination reaction of *cis*- or *trans*-diphenyl(styryl)phosphine and diphenylphosphine promoted by the chiral organopalladium complex (*S*)-**60** (Scheme 5.1) was carried out at -78 °C in the presence of a catalytic amount of NEt₃. The reaction gave a 2.9 :1 mixture of diastereomers **181a** and **181b**, respectively. The ³¹P {¹H}NMR spectrum of the crude product in CDCl₃ showed two major doublet resonance signals at δ 49.9 and 45.9 (*J*_{PP} = 38.2 Hz). The two minor doublet appeared at 49.5 and 47.6 (*J*_{PP} = 34.3 Hz). Unfortunately the two diastereomers always co-crystallized together in the 1:1 ratio. Upon the removal of the chiral auxiliary, a racemic mixture of the dichloro complexes was obtained.

Scheme 5.1

The X-ray crystallography affirms that two independent molecules are in one asymmetric unit. The two molecules not only differ in relative bond lengths and angles but also in the absolute configuration of the chiral carbon centres (C_{16} and C_{62}). The molecular structure of complex **181a** was given in Figure 5.1, which has an *S* absolute configuration at the newly formed chiral carbon centre C_{16} and the molecular structure of complex **181b** was given in Figure 5.2, which has an *R* absolute configuration at the newly formed chiral carbon centre C_{62} . The geometry at Pd_1 is slightly distorted square plane with a distortion angle of 2.0° and a mean deviation from planarity of $0.013 \text{ \AA}$; the newly formed five-membered ring is found to adopt λ ring conformation. On the other hand, the geometry at Pd_2 is significantly distorted square plane with a distortion angle of 13.2° and a mean deviation from planarity of $0.165 \text{ \AA}$; the newly formed five-membered ring is found to adopt δ ring conformation. Based on the X-ray crystallography studies, it is apparent that the complex **181b** adopting a δ ring conformation is a sterically unfavorable structure as it shows a significant distortion angle of the geometry at palladium(II) centre and significant deviation from the planarity.

Figure 5.1 Crystal Structure of Complex (*S,S*)-181a

Figure 5.2 Crystal Structure of Complex (*S,R*)-**181b**

Table 5.1 Selected Bond Lengths (Å) and Angles (deg) for Complexes **181**

Pd(1)-C(1)	2.073(3)	Pd(1)-N(1)	2.073(3)
Pd(1)-P(1)	2.359(1)	Pd(1)-P(2)	2.244(1)
Pd(2)-C(47)	2.065(3)	Pd(2)-N(2)	2.136(3)
Pd(2)-P(4)	2.236(1)	Pd(2)-P(3)	2.368(1)
P(1)-C(16)	1.863(3)	P(2)-C(15)	1.842(3)
P(3)-C(62)	1.871(4)	P(4)-C(61)	1.839(4)
C(1)-Pd(1)-N(1)	80.2(1)	C(1)-Pd(1)-P(2)	95.1(1)
N(1)-Pd(1)-P(2)	175.3(1)	C(1)-Pd(1)-P(1)	178.0(1)
N(1)-Pd(1)-P(1)	100.2(1)	P(1)-Pd(1)-P(2)	84.5(1)
C(47)-Pd(2)-N(2)	80.1(1)	C(47)-Pd(2)-P(4)	95.4(1)
N(2)-Pd(2)-P(4)	170.2(9)	C(47)-Pd(2)-P(3)	170.9(1)
N(2)-Pd(2)-P(3)	101.2(1)	P(4)-Pd(2)-P(3)	84.7(1)

Initially, with the limited spectroscopic and structural information, it was impossible to assign the ^{31}P $\{^1\text{H}\}$ NMR signals to a particular isomer or identify which diastereomer is the major product. However, this could be achieved by the analysis of the X-ray structural feature of both complexes together with a model study. The study of the absolute conformation of the “PdC₃N” ring and the newly formed five-membered “PdP₂C₂” ring and the staggered orientation of the P and N substituents in each diastereomer may offer an opportunity for the understanding of the difference between λ and δ ring conformation at the newly formed five-membered “PdP₂C₂” ring. As discussed in Chapter 1, the five-membered ring conformation of the *S*-palladium template (*S*)-**60** is locked into λ ring conformation rigidly, so that the two methyl substituents at the nitrogen atom of the palladium(II) template are locked into the non-equivalent axial and equatorial positions (Fig. 5.1). Similarly the λ ring conformation in complex **181a** forces the two phenyl substituents at P to adopt an axial and an equatorial position. As shown in Fig. 5.1,

projection of the P and N substituents in complex **181b** illustrated a significant steric repulsion between the methyl and phenyl substituents in both axial positions. Furthermore, the methyl and phenyl substituents in the equatorial positions suffer severe steric congestion. In contrast, the specific steric repulsion within complex **181a** adopting a λ ring conformation could easily avoid all major steric repulsions by slightly distorting the square plane of the palladium(II) centre. Thus the major product in Scheme 5.1 must be complex **181a** and the minor product must be complex **181b**. Therefore the ^{31}P $\{^1\text{H}\}$ NMR assigning of these two diastereomers can be achieved.

Fig. 5.1

complex **181a**
sterically favorable

staggered orientation of the
P and N substituents in complex **181a**

complex **181b**
sterically unfavorable

staggered orientation of the
P and N substituents in complex **181b**

5-2.2 Hydrophosphination Reaction of Diphenylphosphine and DMAD

The hydrophosphination reaction between diphenylphosphine and DMAD (dimethyl acetylene dicarboxylate) could be performed in dry diethyl ether without any catalysts giving a racemic buff-colored diphosphine ligand after four days¹³⁸. The process could also be catalyzed by achiral complexes $\text{Fe}^{139\text{a}}$, or Cr, Mo^{139b} complexes generating the same racemic ligand. On the other hand, with the chiral palladium(II) template (*S*)-**60**, this addition reaction could be completed within 2 hours in dichloromethane at room temperature, giving an enantiomerically enriched diphosphine ligand. Furthermore, the reaction was found to proceed with higher stereo-selectivity when the reaction was conducted at -78°C initially (Scheme 5.2). The presence of a catalytic amount of NEt_3 is crucial for avoiding side products and generating two products with a good selectivity. Theoretically there should be four diastereomeric products with the two newly generated chiral carbon centres adopting the (*RS*), (*RR*), (*SR*) and (*SS*) configurations. However in both the (*RS*) and (*SR*) diastereomers one of the ester substituent must occupy a steric unfavorable axial position, regardless of the conformation adopted by the five-membered ring. On the other hand, in both the (*RR*) and (*SS*) diastereomers, all the ester substituents can occupy the sterically favourable equatorial position. Accordingly diastereomers **183a** and **183b** were the only two products obtained in the asymmetric reaction. Since the naphthyl auxiliary was locked to be λ ring conformation, arising from the inter-chelate repulsion, the newly formed five-membered P-P ring at the palladium(II) centre prefers to adopt λ ring conformation, thus the major product must be **183a**. The two products could not be separated by column chromatography. They always came out together at the ratio of 1:6. The mixture showed two sets of two doublet $^{31}\text{P} \{^1\text{H}\}$ NMR signals at δ 36.6, 57.4 ($J_{\text{pp}} = 37.8$ Hz, minor) and 36.1, 55.3 ($J_{\text{pp}} = 39.0$ Hz, major). Neither of the two diastereomers could be isolated in its enantiomerally pure form. Consequently the naphthylamine

auxiliary was removed from the diastereomers by conc. hydrochloric acid. The enantiomerically enriched isomer (*R,R*)-**184** was subsequently obtained as yellow crystals via fractional crystallization from dichloromethane and diethyl ether. Isomer (*R,R*)-**184** showed a singlet resonance signal at δ 58.1 in the ^{31}P $\{^1\text{H}\}$ NMR spectrum (in CDCl_3).

Scheme 5.2

The isolated isomer was analyzed by X-ray crystallography (Figure 5.3) and confirmed that only one isomer existed in the molecule, which is (*R,R*)-**184**. The bond lengths and angles are summarized in Table 5.2. The crystal structure affirmed that both of the chiral carbon centres (C_1 and C_2) substituted by ester groups adopt the *R* configuration, and the five-membered diphosphine chelate adopts the λ ring conformation with the two ester groups adopting sterically favorable equatorial positions. The geometry at palladium(II) is slightly distorted square plane with a distortion angle of 6.4° and a mean deviation from planarity of $0.087 \text{ \AA}$. The intraligand angles at the palladium atom were $P_1\text{-Pd-}P_2$ $87.4(1)^\circ$ and $Cl_1\text{-Pd-}Cl_2$ $93.8(1)^\circ$ and the interligand angles were $Cl_1\text{-Pd-}P_1$ $91.0(1)^\circ$ and $Cl_2\text{-Pd-}P_2$ $88.1(1)^\circ$.

Figure 5.3 Crystal Structure of Dichloro Complex (*R,R*)-184

Table 5.2 Selected Bond Lengths (Å) and Angles (deg) for Dichloro Complex (*R,R*)-**184**

Pd(1)-Cl(1)	2.353(2)	Pd(1)-Cl(2)	2.346(2)
Pd(1)-P(1)	2.239(2)	Pd(1)-P(2)	2.228(2)
O(1)-C(4)	1.329(6)	O(1)-C(6)	1.434(7)
O(2)-C(4)	1.200(6)	O(3)-C(3)	1.195(6)
O(4)-C(3)	1.341(6)	O(4)-C(5)	1.458(7)
P(1)-C(1)	1.864(5)	P(2)-C(2)	1.868(5)
C(1)-C(2)	1.534(6)	P(2)-Pd(1)-P(1)	87.44(6)
P(2)-Pd(1)-Cl(2)	88.1(1)	P(1)-Pd(1)-Cl(2)	174.4(1)
P(2)-Pd(1)-Cl(1)	174.1(1)	P(1)-Pd(1)-Cl(1)	91.0(1)
Cl(2)-Pd(1)-Cl(1)	93.8(1)	C(1)-P(1)-Pd(1)	107.0(2)
C(2)-P(2)-Pd(1)	106.7(2)		

Further treatment of complex (*R,R*)-**184** with aqueous cyanide liberated the C_2 symmetrical bi-dentate phosphine ligand (*S,S*)-**185** as white solid in quantitative yield, $[\alpha]_D^{25} -50^\circ$ (*c* 0.3 CH_2Cl_2) (Scheme 5.2). The $^{31}P \{^1H\}$ NMR spectrum of this free ligand showed a singlet resonance signal at δ -6.2. The optical purity of ligand (*S,S*)-**185** [*i.e.* also the dichloro complex (*R,R*)-**184**] was established by recoordination of the liberated free ligand to (*S*)-**60** and the equally available enantiomeric complex (*R*)-**60** separately. Re-complexation of (*S,S*)-**185** to (*S*)-**60** gave only one product **183a** (Scheme 5.2), exhibiting a set of two doublet resonance signals at δ 36.1 and 55.3 in $^{31}P \{^1H\}$ NMR spectrum. It is noteworthy that the phosphorus resonance signals are identical to the one recorded for the major product in the product mixture obtained directly from the hydrophosphination reaction. Reoordination of free ligand to (*R*)-**60** similarly generated only one product **186**, which is the enantiomeric form of **183b**, exhibiting a set of two doublet resonance signals at δ 36.6 and 57.4 in $^{31}P \{^1H\}$ NMR spectrum. It is noteworthy that the phosphorus resonance signals are identical to the one recorded for the minor product in the product mixture obtained directly from the hydrophosphination reaction.

Importantly, since the phosphorus resonance signals at δ 36.1 and 55.3 were not observed, this NMR study confirmed the optical purity of the liberated phosphine-phosphine oxide ligand (*S,S*)-**185** [and also (*R,R*)-**184**]. From these recoordination experiments, spectroscopic and crystallographic studies, the two stereoisomeric products generated in the chiral metal template promoted hydrophosphination reaction of DMAD have been established unambiguously to be complexes **183a** (major) and **183b** (minor), as predicted by the model study.

It should be noted that the liberated ligand will lose its chirality by giving optical rotation values close to zero in different wavelength, in a basic condition. We propose that in basic solution deprotonation occurs for the chiral carbon atoms. Since there are no any chiral auxiliaries in the liberated ligand, thus the free protons will subsequently attack the negative charged carbon centres from either directions, thereafter the two carbon centres lose their chirality. It is possible that during the isomerization process, *meso*-isomers could be resulted as intermidates. However in the *meso*-isomer ligand, one of the ester substituent must occupy a steric unfavorable axial position, it would be facile to isomerize to a C_2 symmetric ligand, in which both ester substituents can occupy the sterically favourable equatorial positions.

5-3 Conclusion

In summary, the hydrophosphination reaction of diphenylphosphine and *cis*- or *trans*-diphenyl(styryl)phosphine promoted by a chiral palladium template was demonstrated in this chapter. The isolated isomer was found to be a mixture of two diastereomeric products, which have different chiralities at the newly formed chiral carbon atoms. The corresponding liberated free ligand was found to exist in its racemic form. Meanwhile, hydrophosphination reaction of diphenylphosphine and DMAD promoted by a chiral palladium template was also demonstrated in this chapter. The resulting diastereomeric products could not be separated into their stereoisomeric pure form.

Nevertheless, after the removal of the naphthylamine auxiliary, the resulting dichloro neutral complex was enriched in the one optically active form. The enriched isomer could be eventually isolated in its enantiomerically pure form, from which the corresponding free ligand could be liberated stereospecifically.

5-4 Experimental Section

Attempt to synthesis of [SP-4-4-{(S)-1-[1-(dimethylamino)ethyl]naphthyl-C²,N} {(S)- or (R)-1-phenyl-1,2-bis(diphenylphosphino)ethane-P¹,P²}] palladium(II) perchlorate, 181. Complex (S)-60 (0.841g, 1.7mmol) and *cis-* or *trans*-diphenyl(styryl)phosphine (0.470g, 1.7mmol) were dissolved in 30 mL dichloromethane and cooled down to -78 °C; PPh₂H (0.314g) was dissolved in 20 mL CH₂Cl₂ and cooled down to -78 °C, subsequently transferred to the mixture followed by adding catalytic amount of NEt₃. Diastereomeric complexes **181** were co-crystallized with 1:1 ratio from dichloromethane and diethyl ether as colourless crystal 0.445 (30%, yield).

Attempt to synthesis of [SP-4-3-dichloro{(S)- or (R)-1-phenyl-1,2-bis(diphenylphosphino)ethane-P¹,P²}] palladium(II), 182. To the solution of complex **181** (0.215g, 0.3mmol) in dichloromethane, 15ml of conc. hydrochloric acid was added. After vigorous stirring overnight, the mixture was extracted with water (3 x 30 mL) and dried with MgSO₄. Complex **182** was crystallized in dichloromethane and diethyl ether as yellow crystals [α]_D 0° (*c* 0.30 CH₂Cl₂); 0.144g (80% yield). ³¹P {¹H}NMR (CDCl₃) δ 42.7 (s), 73.6 (s); ¹H NMR (CDCl₃) δ 2.70-2.97 (m, 2H, CHCH₂); 3.93-4.00 (m, 1H, CHCH₂); 7.03-7.62 (m, 25H, aromatics).

Attempt to synthesize of [SP-4-3-dichloro{(R, R)-bis(dephenylphosphino)-1,2-bis(methylcarboxylato) ethane-P¹,P²}] palladium(II), (R,R)-184. Complex (S)-60 (1.315g, 2.7mmol) and DMAD (0.384g, 2.7mmol) were dissolved in 30 mL dichloromethane and cooled down to -78 °C; PPh₂H (1.007g, 5.4mmol)

was dissolved in 20 mL CH_2Cl_2 and cooled down to $-78\text{ }^\circ\text{C}$, and subsequently transferred to the mixture of (*S*)-**60** and DMAD followed by adding catalytic amount of NEt_3 . The whole mixture was stirred until the temperature gradually increased to room temperature and 15 mL of conc. hydrochloric acid was added for vigorous stirring overnight followed by extraction with distilled water ($3 \times 30\text{ mL}$) and drying with MgSO_4 . Complex (*R,R*)-**184** was crystallized carefully from dichloromethane and diethyl ether as light yellow crystals: mp $252\text{--}253\text{ }^\circ\text{C}$; $[\alpha]_{\text{D}} +130$ ($c\ 0.3$, CH_2Cl_2); 0.75g (40%, yield). Anal. Calcd for $\text{C}_{31}\text{H}_{30}\text{Cl}_4\text{O}_4\text{P}_2\text{Pd}$: C, 47.9; H, 3.9. Found C, 47.7; H, 3.8. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ 58.1 (s, 2P, P); ^1H NMR (CDCl_3) δ 3.38 (s, 6H, 2CH_3), 4.20 (d, 2H, $J_{\text{PH}} = 6.5\text{ Hz}$, 2CH), 7.55–7.73 (m, 20H, aromatics).

Liberation of (*S,S*)-dimethyl-1,2-bis-(diphenylphosphino)-1,2-ethanedicarboxylate, (*S,S*)-185**.** A solution of (*R,R*)-**184** (0.044g, 0.1mmol) in dichloromethane (30 mL) was stirred vigorously with a saturated aqueous solution of potassium cyanide (1g) for 1 hour. The resulting colourless organic layer was separated, washed with water, and dried with MgSO_4 . Upon removal of solvent, a white solid was obtained: $[\alpha]_{\text{D}} -50^\circ$ ($c\ 0.3\ \text{CH}_2\text{Cl}_2$); 0.028g (85% yield). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ -6.2 (s, 2P, P); ^1H NMR (CDCl_3) δ 3.81 (s, 6H, 2CH_3), 4.43 (d, 2H, $J_{\text{PH}} = 9.0\text{ Hz}$, 2CH), 7.17–7.94 (m, 20H, aromatics).

Typical procedure used for the re-complexation reactions. Stoichiometric amounts of complex (*S*)-**60** or (*R*)-**60** and free ligand (*S,S*)-**185** were stirred in dichloromethane separately at room temperature and the solution was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy until equilibrium was established.

Crystal Structure Determination. Complexes **181** and (*R,R*)-**184** were analyzed at Nanyang Technological University.

CONCLUSION

The thesis investigates the application of the chiral palladium(II) complex having an optically active naphthylamine auxiliary in stoichiometric reaction to prepare enantiomerically pure functionalized phosphine ligands. The square planar geometry of palladium(II) centre makes only four coordination sites available. As two of the four coordination sites are occupied by a nitrogen donor and a carbon atom within the naphthylamine auxiliary, the coming triphosphine ligand would function as bidentate chelate leaving one phosphine unit dangling freely, which can be subsequently oxidized. Due to the rigidity of Pd-P bonds, the two coordinated phosphorus units will not react with oxidation reagent. As such, the prochiral centre in the triphosphine ligand becomes a chiral one even without the palladium stabilization, due to the transformation of a free phosphine to a phosphine oxide, sulfide or selenide.

A five-membered ring is facile to be formed during the coordination process, which significantly reduces the number of diastereomeric products in the crude mixture. The corresponding X-ray single diffraction spectroscopy of the isolated optically pure palladium(II) complexes affirms square planar geometry of palladium centres with small distortion angles and mean deviation.

The chiral palladium(II) template is an efficient chirality inducer in the stoichiometric reaction discussed in the thesis, and it works effectively in both regio- and stereo-selectivity. The chirality and the design of the chiral naphthylamine auxiliary make the five-membered ring within the palladium(II) template to be locked into a λ ring conformation in both solid form and solution. The specific λ ring conformation is subsequently induced the corresponding products having a λ ring conformation in the newly formed five-membered ring of the bidentate phosphine chelate to be predominantly generated. The corresponding

X-ray single diffraction spectroscopy of the isolated optically pure palladium(II) complexes also affirms the λ ring conformation. In addition, the asymmetric coordination sites within the naphthylamine auxiliary play an important role in both regio- and stereo-selectivity in the newly formed five-membered bidentate phosphine chelate. Especially the chiral phosphorus atom within the triphosphine ligand will occupy the coordination site that is *trans* to the nitrogen donor. Besides, the effects of the asymmetric coordination sites within the naphthylamine auxiliary can be observed in $^{31}\text{P} \{^1\text{H}\}$ NMR spectroscopy, in which the coordination shift of the phosphorus atoms *trans* to the nitrogen donor is much significant.

Some of prospect projects are proposed in order to refine some parts, or to continue studying and exploring the potential values of the whole project. By adding diphenylarsine into 1,1-bis(diphenylphosphino)ethene under the presence of the palladium(II) template, a non-symmetrical five-membered chelate (P-As) having a dangling freely diphenylphosphine moiety would be generated. Due to the different properties of the two available coordination sites of the palladium(II) template, the phosphorus donor group would be facile to occupy the position *trans* to nitrogen atom, while the arsine donor group would be facile to occupy the position *cis* to nitrogen atom. This would subsequently reduce the number of resulted products. Meanwhile addition of ligands containing nitrogen or sulfur atoms into 1,1-bis(diphenylphosphino)ethylene could be used to prepare phosphorus-hetero atom ligands. Also the phosphorus donor group would be facile to occupy the position *trans* to nitrogen atom, which in turn would reduce the number of resulted products. In addition, by changing the substituents at the acetylene (chapter 5, Scheme 5.2), or replacing diphenylphosphine with other secondary phosphine ligands, bidentate phosphine ligands with a variety of functional groups could be prepared.

In conclusion, the chiral palladium(II) template can function efficiently and effectively as reaction promoter, resolving reagent, chirality inducer in stoichiometric

selective oxidation and hydrophosphination reaction to prepare optically pure functionalized bidentate phosphine ligands. The application in selective oxidation reaction can create a chiral centre in a prochiral tridentate ligand in two steps: coordination of the specific tridentate ligand followed by oxidation of the uncoordinated unit. Compared with chiral phosphine ligands generated by previously discussed methods such as Diels-Alder reactions (Chapter 1, 1-3.4), the resulted chiral phosphine ligands are with more diversified functional groups like phosphine oxide or phosphine sulfide. However the selective oxidation reaction can only work in tridentate ligands, and the ligands should function as bidentate chelate leaving one uncoordinated unit which can be subsequently oxidized. Additionally the application of hydrophosphination reaction in organic triple bond is much easier in handling in preparing chiral bidentate phosphine ligands compared with hydrophosphination reaction in vinylphosphine, as it can avoid of separation of *cis* and *trans* vinylphosphine ligands. However reaction would only perform smoothly if the C-C triple bond is substituted by electron withdrawing groups. For example PhCCPh is not reactive to this reaction as the phenyl groups would conjugate with C-C triple bond during reacting process.

REFERENCES

1. Dupont, J. Consorti, C. S.; Spencer, J. *Chem. Rev.* **2005**, *105*, 2527.
2. Sololov, V. I.; Sorokina, T. A.; Troitskaya, L. L.; Solovieva, L. I.; Reutov, O. A. *J. Organometal. Chem.* **1972**, *36*, 389.
3. (a) Sololov, V. I.; Bashilov, V. V.; Musaev, A. A.; Reutov, O. A. *J. Organometal. Chem.*, **1982**, *225*, 57. (b) Sololov, V. I.; Reutov, O. A. *Coord. Chem. Rev.* **1978**, *27*, 189.
4. Spencer, J; Maassarani, F.; Pfeffer, M. *Tetrahedron: Asymmetry*, **1994**, *5*, 321.
5. (a) Arlen, C.; Pfeffer, M.; Bars, O.; Grandjean, D. *J. Chem. Soc., Dalton Trans.* **1983**, 1535. (b) Abicht, H. P.; Issleib, K. *J. Organomet. Chem.* **1978**, *149*, 209. (c) Abicht, H. P.; Issleib, K. *J. Organomet. Chem.* **1985**, *289*, 201
6. Maassarani, F.; Pfeffer, M.; Borgne, G. L.; Jastrzebski, J. T. B. H.; van Koten, G. *Organometallics* **1987**, *6*, 1111.
7. Dunina, V. V.; Gorunova, O. N.; Kuz'mina, L. G.; Livantsov, M. V. Grishin, Y. K. *Tetrahedron: Asymmetry*, **1999**, *10*, 3951.
8. Morales-Morales, D.; Cramer, R. E.; Jensen, C. M. *J. Organometal. Chem.*, **2002**, *654*, 44.
9. Dupont, J.; Gruber, A. S.; Fonseca, G. S.; Monteiro, A. L.; Ebeling, G. *Organometallics* **2001**, *20*, 171.
10. Tani, K.; Brown, L. D.; Ahmed, J.; Ibers, J. A.; Yokota, M.; Nakamura, A.; Otsuka, S. *J. Am. Chem. Soc.* **1977**, *99*, 7876.
11. Roberts, N. K.; Wild, S. B. *J. Chem. Soc., Dalton Trans.* **1979**, 2015.
12. Gül, N.; Nelson, J. H. *Tetrahedron* **2000**, *56*, 71.

13. Allen, D. G.; McLaughlin, G. M.; Robertson, G. B.; Steffen, W. L.; Salen, G.; Wild, S. *B. Inorg. Chem.* **1982**, *21*, 1007.
14. Li, Y.; Ng, K.-H.; Selvaratnam, S.; Tan, G.-K.; Vittal, J. J.; Leung, P.-H. *Organometallics* **2003**, *22*, 834.
15. Dunina, V. V.; Razmyslova, E. D.; Gorunova, O. N.; Livantsov, M. V.; Grishin, Y. K. *Tetrahedron: Asymmetry*, **2003**, *14*, 2331.
16. Fuchita, Y.; Yoshinaga, K.; Ikeda, Y.; Kinoshita-Kawashima, J. *J. Chem. Soc., Dalton Trans.* **1997**, 2495.
17. Peterson, D. L.; Keuseman, K. J.; Kataeva, N. A.; Kuz'mina, L. G.; Howard, J. A. K.; Dunina, V. V.; Smoliakova, I. P. *J. Organometal. Chem.*, **2002**, *654*, 66.
18. Marinetti, A.; Hubert, P.; Genêt, J.-P. *Eur. J. Org. Chem.* **2000**, 1815.
19. Li, Y.; Selvaratnam, S.; Yittal, J. J.; Leung, P.-H. *Inorg. Chem.* **2003**, *42*, 3229.
20. Ng, J. K.-P.; Tan, G.-K.; Yittal, J. J.; Leung, P.-H. *Inorg. Chem.* **2003**, *42*, 7674.
21. Zhao, G.; Wang, Q.-G.; Mak, T. C. W. *Polyhedron* **1998**, *18*, 577.
22. Zhao, G.; Wang, Q.-G.; Mak, T. C. W. *Tetrahedron: Asymmetry*, **1998**, *9*, 1557.
23. López, C.; Bosque, R.; Solans, X.; Font-Bardia, M. *Tetrahedron: Asymmetry*, **1996**, *7*, 2527.
24. Zhao, G.; Xue, F.; Zhang, Z.-Y.; Mak, T. C. W. *Organometallics* **1997**, *16*, 4023.
25. Zhao, G.; Wang, Q.-G.; Mak, T. C. W. *Tetrahedron: Asymmetry*, **1998**, *9*, 2253.
26. (a) Cui, X. L.; Wu, Y. J.; Du, C. X.; Yang, L. R.; Zhu, Y. *Tetrahedron: Asymmetry*, **1999**, *10*, 1255. (b) Wu, Y. J.; Cui, X. L.; Du, C. X.; Wang, W. L.; Guo, R. Y.; Chen, R. *F. J. Chem. Soc., Dalton Trans.* **1998**, 3727.
27. Dunina, V. V.; Gorunova, O. N.; Livantsov, M. V.; Grishin, Y. K.; Kuz'mina, L. G.; Kataeva, N. A.; Churakov, A. V. *Tetrahedron: Asymmetry*, **2000**, *11*, 3967.
28. Benito, M.; López, C.; Solans, X.; Font-Bardía, M. *Tetrahedron: Asymmetry*, **1998**, *9*, 4219.

29. Sokolov, V. I.; Troitskaya, L. L.; Reutov, O. A. *J. Organometal. Chem.*, **1979**, 182, 537.
30. Otsuka, S.; Nakamura, A.; Kano, T.; Tani, K. *J. Am. Chem. Soc.* **1971**, 93, 4301.
31. Wild, S. B. *Coord. Chem. Rev.* **1997**, 166, 291.
32. (a) Pietrusiewicz, K. M.; Zablocka, M. *Chem. Rev.* **1994**, 94, 1375. (b) Casalnuovo, A. L.; Rajanbabu, T. V.; Ayers, T. A.; Warren, T. H. *J. Am. Chem. Soc.* **1994**, 116, 9869. (c) Schnyder, A.; Hintermann, L.; Togni, A. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 931. (d) Brown, J. M.; Hulmes, D. I.; Layzell, T. P. J. *J. Chem. Soc., Chem. Commun.* **1993**, 1673.
33. Dunina, V. V.; Golovan, E. B. *Tetrahedron: Asymmetry*, **1995**, 6, 2747.
34. Gugger, P.; Willis, A. C.; Wild, S. B. *J. Chem. Soc., Chem. Commun.* **1990**, 1169.
35. (a) Baechler, R. D.; Mislou, K. *J. Am. Chem. Soc.* **1971**, 93, 773. (b) Pietrusiewicz, K. M.; Zablocka, M. *Chem. Rev.* **1994**, 94, 1375.
36. (a) Horner, L.; Jordan, M. *Phosphorus Sulfur Relat. Elem.* **1980**, 8, 235. (b) Omelańczuk, J. *J. Chem. Soc., Chem. Commun.* **1992**, 1718.
37. Pabel, M.; Willis, A. C.; Wild, S. B. *Tetrahedron: Asymmetry*, **1995**, 6, 2369.
38. (a) Roberts, N. K.; Wild, S. B. *J. Am. Chem. Soc.* **1979**, 101, 6254. (b) Gabbittas, N.; Salem, G.; Sterns, M.; Willis, A. C. *J. Chem. Soc., Dalton. Trans.* **1993**, 3271. (c) Leitch, J.; Salem, G.; Hockless, D. C. R. *J. Chem. Soc., Dalton. Trans.* **1995**, 649. (d) Chatterjee, S.; George, M. D.; Salem, G.; Willis, A. C. *J. Chem. Soc., Dalton. Trans.* **2001**, 1890. (e) He, G.; Mok, K. F.; Leung, P. -H. *Organometallics* **1999**, 18, 4027.
39. Salem, G.; Wild, S. B. *Inorg. Chem.* **1983**, 22, 4049.
40. Doyle, R. J.; Salem, G.; Willis, A. C. *J. Chem. Soc., Dalton. Trans.* **1995**, 1867.
41. Barclay, C. E.; Deeble, G.; Doyle, R. J.; Elix, S. A.; Salem, G.; Jones, T. L. B.; Wild, S. B.; Willis, A. C. *J. Chem. Soc., Dalton. Trans.* **1995**, 57.
42. Martin, J. W. L.; Palmer, J. A. L.; Wild, S. B. *Inorg. Chem.* **1984**, 23, 2664.

43. Leung, P. -H.; Quek, G. H.; Lang, H.; Liu, A. M.; Mok, K. F.; White, A. J. P.; Williams, D. J.; Rees, N. H.; McFarlane, W. J. *Chem. Soc., Dalton. Trans.* **1998**, 1639.
44. Lutz, R. *Chem. Rev.* **1984**, 84, 205.
45. Overman, L. E. *Acc. Chem. Rev.* **1980**, 13, 218.
46. Beak, P.; Bonham, J.; Lee, J. T. *J. Am. Chem. Soc.* **1968**, 90, 1569.
47. (a) Overman, L. E. *J. Am. Chem. Soc.* **1974**, 96, 597. (b) Overman, L. E. *J. Am. Chem. Soc.* **1976**, 98, 2901.
48. (a) Vyas, D. M.; Chiang, Y.; Doyle, T. W. *J. Org. Chem.* **1984**, 49, 2037. (b) Hauser, F. M.; Ellenberger, S. R.; Glusker, J. P.; Smart, C. J.; Carrell, H. L. *J. Org. Chem.* **1986**, 51, 5024. (c) Roush, W. R.; Straub, J. A.; Brown, R. J. *J. Org. Chem.* **1987**, 52, 5127. (d) Flynn, D. L.; Becker, D. P.; Nosal, R.; Zabrowski, D. L. *Tetrahedron Lett.* **1992**, 33, 7283. (e) Chen, A.; Savage, I.; Thomas, E. J.; Wilson, P. D. *Tetrahedron Lett.* **1993**, 34, 6769. (f) Casara, P. *Tetrahedron Lett.* **1994**, 35, 3049. (g) Bamba, M.; Nishikawa, T. Isobe, M. *Tetrahedron* **1998**, 54, 6639.
49. Pearson, R. G. *Hard and Soft Acids and Bases*, Hutchinson and Ross, Stroudsburg, PA, 1973.
50. Overman, L. E. *Angew. Chem., Int. Ed. Engl.*, **1984**, 23, 579.
51. (a) Calter, M.; Hollis, T. K.; Overman, L. E.; Ziller, J.; Zipp, G. G.; *J. Org. Chem.* **1997**, 62, 1449. (b) Uozumi, Y.; Kato, K.; Hayashi, T. *Tetrahedron Asymmetry*, **1998**, 9, 1065.
52. Kuzmina, L. G.; Struchkov, Y. T.; Troitskaya, L. L.; Jokolov, V. I.; Reumov, O. A., *Izv. Akad. Nauk. SSSR, Ser, Khim.* **1979**, 1528.
53. Cohen, F.; Overman, L. E. *Tetrahedron Asymmetry*, **1998**, 9, 3213.
54. .Donde, Y.; Overman, L. E. *J. Am. Chem. Soc.* **1999**, 121, 2933.

55. (a) Overman, L. E.; Remarchuk, T. P. *J. Am. Chem. Soc.* **2001**, *124*, 12. (b) Anderson, C. E. Donde, Y.; Douglas, C. J.; Overman, L. E. *J. Org. Chem.* **2005**, *70*, 648.
56. Overman, L. E.; Owen, C. E.; Zipp, G. G. *Angew. Chem., Int. Ed.* **2002**, *41*, 3884.
57. (a) Overman, L. E.; Owen, C. E.; Pavan, M. M. *Org. Lett.* **2003**, *5*, 1809. (b) Kirsch, S. F.; Overman, L. E.; Watson, M. P. *J. Org. Chem.* **2004**, *69*, 8101.
58. (a) Stevens, A. M.; Richards, C. J. *Organometallics* **1999**, *18*, 1346. (b) Jones, G.; Richards, C. J. *Organometallics* **2001**, *20*, 3884.
59. (a) Kirsch, S. F.; Overman, L. E. *J. Org. Chem.* **2005**, *70*, 2859. (b) Prasad, R. S.; Anderson, C. E.; Richards, C. J.; Overman, L. E. *Organometallics* **2005**, *24*, 77. (c) Kirsch, S. F.; Overman, L. E. *J. Am. Chem. Soc.* **2005**, *127*, 2866. (d) Anderson, C. E.; Overman, L. E. *J. Am. Chem. Soc.* **2003**, *125*, 12412.
60. (a) Bedford, R. B. *J. Chem. Soc., Chem. Commun.* **2003**, 1787. (b) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759. (c) Albrecht, M.; Kocks, B. M.; Spek, A. L.; van Koten, G. *J. Organomet. Chem.* **2001**, *624*, 271. (d) Dupont, J.; Pfeffer, M.; Spencer, J. *Eur. J. Inorg. Chem.* **2001**, 1917.
61. Ito, Y.; Sawamura, M.; Hayashi, T. *J. Am. Chem. Soc.* **1986**, *108*, 6405.
62. (a) Nesper, R.; Pregosin, P. S.; Püntener, K.; Wörle, M. *Helv. Chim. Acta* **1993**, *76*, 2239. (b) Nesper, R.; Pregosin, P. S.; Püntener, K.; Wörle, M.; Albinati, A. *J. Organomet. Chem.* **1996**, *507*, 85.
63. Longmire, J. M.; Zhang, X. *Organometallics* **1998**, *17*, 4374.
64. Williams, B. S.; Dani, P.; Lutz, M.; Spek, A. L.; van Koten, G. *Helv. Chim. Acta* **2001**, *81*, 3519.
65. (a) Ramachandran, P. V.; Chen, G. -M.; Lu, Z. -H.; Brown, H. C. *Tetrahedron Lett.* **1996**, *37*, 3795. (b) McKinsty, L.; Livinghouse, T. *Tetrahedron* **1995**, *51*, 7655.
66. (a) Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusomoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244. (b) Wolfe, B.; Livinghouse, T. *J. Am. Chem. Soc.* **1998**, *120*, 5116.

67. Takenaka, K.; Uozumi, Y. *Org. Lett.* **2004**, 6, 1833.
68. Harris, T. D.; Neuschwander, B.; Boekelheide, V. *J. Org. Chem.* **1978**, 43, 727.
69. Stark, M. A.; Jones, G.; Richards, C. J. *Organometallics* **2000**, 19, 1282.
70. Motoyama, Y.; Koga, Y.; Kobayashi, K.; Aoki, K.; Nishiyama, H. *Chem. Eur. J.* **2002**, 8, 2968.
71. (a) de Meijere, A.; Meyer, F. E. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 2379. (b) Morales-Morales, D.; Cramer, R. E.; Jensen, C. M. *J. Organomet. Chem.* **2002**, 654, 44. (c) Shaw, B. L.; Perera, S. D.; Staley, E. A. *J. Chem. Soc., Chem. Commun.* **1998**, 1361. (d) Shaw, B. L.; Perera, S. D. *Chem. Soc., Chem. Commun.* **1998**, 1863. (e) Reetz, M. T.; Kaufmann, D. E. *Angew. Chem., Int. Ed. Engl.* **2000**, 39, 165. (f) Sato, Y.; Nukui, S.; Sodeoka, M.; Shibasaki, M. *Tetrahedron* **1994**, 50, 371.
72. Bravo, J.; Cativiela, C.; Navarro, R.; Urriolabeitia, E. P. *J. Organomet. Chem.* **2002**, 650, 157.
73. (a) Noyori, R.; Takaya, H. *Acc. Chem. Rev.* **1990**, 23, 345 and references therein. (b) Hayashi, T.; Hayashizaki, K.; Kiyoi, T.; Ito, Y. *J. Am. Chem. Soc.* **1988**, 110, 8153. (c) Hayashi, T.; Konishi, M.; Fukushima, M.; Kanehira, K.; Hioki, T.; Kumada, M. *J. Org. Chem.* **1983**, 48, 2195.
74. Hayashi, T.; Niizuma, S.; Kamikawa, T.; Suzuki, N.; Uozumi, Y. *J. Am. Chem. Soc.* **1995**, 117, 9101.
75. (a) Trost, B. M.; van Vranken, D. L. *Chem. Rev.* **1996**, 96, 395. (b) Rieck, J.; Helmchen, G. *Angew. Chem. Int. Ed. Engl.* **1995**, 34, 2687. (c) Trost, B. M.; Strege, P. E. *J. Am. Chem. Soc.* **1977**, 99, 1649. (d) Trost, B. M.; Murphy, D. J. *Organometallics* **1985**, 4, 1143.
76. Zhu, G.; Terry, M.; Zhang, X. *Tetrahedron Lett.* **1996**, 37, 4475.
77. Longmire, J. M.; Zhang, X. *Tetrahedron Lett.* **1997**, 38, 1725.

78. (a) Maassarani, F.; Pfeffer, M.; Le Borgne, G. *J. Chem. Soc., Chem. Commun.* **1986**, 488. (b) Maassarani, F.; Pfeffer, M.; Le Borgne, G. *J. Chem. Soc., Chem. Commun.* **1987**, 565. (c) Dupont, J.; Pfeffer, M. *J. Organomet. Chem.* **1987**, 321, C13.
79. Spencer, J.; Pfeffer, M. *Tetrahedron: Asymmetry* **1995**, 6, 419.
80. Gül, N.; Nelson, J. H. *Organometallics* **2002**, 21, 2041.
81. Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1987**, 26, 275.
82. (a) Zhao, G.; Wang, Q. –G.; Mak, T. C. W. *J. Organomet. Chem.* **1999**, 574, 311. (b) Zhao, G.; Yang, Q. –C.; Mak, T. C. W. *Organometallics* **1999**, 18, 3623.
83. Leung, P. –H. *Acc. Chem. Res.* **2004**, 37, 169 and references therein.
84. Leung, P. –H.; Loh, S. –K.; Vittal, J. J.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1997**, 1987.
85. Leung, P. –H.; He, G.; Lang, H.; Liu, A.; Loh, S. –K.; Selvaratnam, S.; Mok, K. F.; White, A. J. P.; Williams, D. J. *Tetrahedron* **2000**, 56, 7.
86. Leung, P. –H.; Lang, H.; Zhang, X.; Selvaratname, S.; Vittal, J. J. *Tetrahedron: Asymmetry* **2000**, 11, 2661.
87. Leung, P. –H.; Qin, Y.; He, G.; Mok, K. F.; Vittal, J. J. *J. Chem. Soc., Dalton Trans.* **2001**, 309.
88. Qin, Y.; Lang, H.; Vittal, J. J.; Tan, G. –K.; Selvaratnam, S.; White, A. J. P.; Williams, D. J.; Leung, P. –H. *Organometallics* **2003**, 22, 3944.
89. He, G.; Loh, S. –K.; Vittal, J. J.; Mok, K. F.; Leung, P. –H. *Organometallics* **1998**, 17, 3931.
90. Leung, P. –H.; Loh, S. –K.; Mok, K. F.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1996**, 591.
91. Leung, P. –H.; Siah, S. –Y.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1998**, 893.
92. Qin, Y.; White, A. J. P.; Williams, D. J.; Leung, P. –H. *Organometallics* **2002**, 21, 171.

93. Song, Y.; Vittal, J. J.; Chan, S. -H.; Leung, P. -H. *Organometallics* **1999**, *18*, 650.
94. (a) Aw, B. -H.; Leung, P. -H. *Tetrahedron: Asymmetry* **1994**, *5*, 1167. (b) Selvaratnam, S.; Leung, P. -H.; White, A. J. P.; Williams, D. J. *J. Organomet. Chem.* **1997**, *542*, 61.
(c) Aw, B. -H.; Leung, P. -H.; White, A. J. P.; Williams, D. J. *Organometallics* **1996**, *15*, 3640.
95. (a) Liu, A.; Mok, K. F.; Leung, P. -H. *J. Chem. Soc., Chem. Commun.* **1997**, 2397. (b) Leung, P. -H.; Liu, A.; Mok, K. F. *Tetrahedron: Asymmetry* **1999**, *10*, 1309.
96. Leung, P. -H.; Selvaratnam, S.; Cheng, C. R.; Mok, K. F.; Rees, N. H.; McFarlane, W. *J. Chem. Soc., Chem. Commun.* **1997**, 751.
97. Song, Y.; Mok, K. F.; Leung, P. -H.; Chan, S. -H. *Inorg. Chem.* **1998**, *37*, 6399.
98. Yeo, W. -C.; Vittal, J. J.; White, A. J. P.; Williams, D. J.; Leung, P. -H. *Organometallics* **2001**, *20*, 2167.
99. Qin, Y.; Selvaratnam, S.; Vittal, J. J.; Leung, P. -H. *Organometallics* **2002**, *21*, 5301.
100. Teo, T. -W.; Selvaratnam, S.; Vittal, J. J.; Leung, P. -H. *Inorg. Chim. Acta* **2003**, *352*, 213.
101. Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2000**, *122*, 9546.
102. Liu, A.; Mok, K. F.; Leung, P. -H. *Organometallics* **2001**, *20*, 3918.
103. Yeo, W. -C.; Tee, S. -Y.; Tan, H. -B.; Tan, G. -K.; Koh, L. L.; Leung, P. -H. *Inorg. Chem.* **2004**, *34*, 8102.
104. (a) Cooper, G. R.; Hassan, F.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Chem. Commun.* **1985**, 614. (b) Cooper, G. R.; McEwan, D. M.; Shaw, B. L. *Inorg. Chim. Acta* **1986**, *122*, 207. (c) Herring, A. M.; Higgins, S. J.; Jacobsen, G. B.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1986**, 882. (d) Hassan, F. S. M.; Higgins, S. J.; Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1988**, 3011. (e) Higgins, S. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1989**, 1527.

105. Bookham, J. L.; Conti, F.; McFarlane, H. C. E.; McFarlane, W. and Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.*, **1994**, 1791.
106. (a) Landis, C. R. and Halpern, J. *J. Am. Chem. Soc.*, **1987**, *109*, 1746. (b) Noyori, R. and Takaya, H. *Acc. Chem. Res.*, **1990**, *23*, 345. (c) Noyori, R. *Chem. Soc. Rev.*, **1989**, *18*, 187. (d) Brunner, H. *J. Organomet. Chem.*, **1986**, *300*, 39. (e) Whitesell, J. K. *Chem. Rev.*, **1989**, *89*, 1581 and refs. Therein.
107. (a) Berners-Price, S. J.; Norman, R. E.; Sadler, P. J. *J. Inorg. Biochem.* **1987**, *31*, 197. (b) Debnath, A. K.; Radigan, L.; Jiang, S. *J. Med. Chem.* **1999**, *42*, 3203.
108. (a) Grushin, V. V. *Organometallics* **2001**, *20*, 3950. (b) Faller, J. W.; Grimmond, B. J.; D'Alliessi, D. G. *J. Am. Chem. Soc.* **2001**, *123*, 2525.
109. (a) Brown, D. H.; Cross, R. J.; Keat, R. *J. Chem. Soc., Dalton Trans.*, **1994**, 1791. (b) Kroshefsky, R. D.; Weiss, R.; Verkade, J. G. *Inorg. Chem.*, **1979**, *18*, 469. (c) Maryanoff, B. E.; Tang, R.; Mislow, K. *J. Chem. Soc., Chem. Commun.* **1985**, 614.
110. Yeo, W. C. ; Tang, L. L.; Yan, B.; Tee, S. Y.; Koh, L. L.; Tan, G. K.; Leung, P. –H. *Organometallics* **2005**, *24*, 5581.
111. Chooi, S. Y. M.; Siah, S. –Y.; Leung, P. –H.; Mok, K. F. *Inorg. Chem.* **1993**, *32*, 4812.
112. Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.
113. (a) Vineyard, B. D.; Knowles, W. S.; Sabacky, M. J.; Bachman, G. L.; Weinkauff, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 5946. (b) Johnson, C. R.; Imamoto, T. *J. Org. Chem.* **1987**, *52*, 2170.
114. Grushin, V. V. *J. Am. Chem. Soc.* **1999**, *121*, 5831 and references therein.
115. Huang, I. D.; Westner, A. A.; Oswald, A. A. Jermansen, T. G. PCT Int. Appl. 8001690, **1980**. Oswald, A. A.; Jermansen, T. G.; Westner, A.; Huang, I. D. U.S. Patent 4687874, **1987**.
116. Terekhova, M. I.; Kron, T. E.; Bondarenko, N. A.; Petrov, E. S.; Tsvetkov, E. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1992**, 2003.

117. Faller, J. W.; Grimmond, B. J.; Curtis, M. *Organometallics* **2000**, *19*, 5174.
118. Gladiali, S.; Pulacchini, S.; Fabbri, D.; Manassero, M.; Sansoni, M. *Tetrahedron: Asymmetry* **1998**, *9*, 391.
119. Sekar, G.; Nishiyama, H. *J. Am. Chem. Soc.* **2001**, *123*, 3603.
120. Grushin, V.V. *J. Am. Chem. Soc.* **1999**, *121*, 5831.
121. Alvarez, B.; Ferná'ndez, E. J.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Lo'pez-de-Luzuriaga, J. M. *Polyhedron* **1998**, *17*, 2029.
122. Vila, J. M.; Pereira, M. T.; Ortigueira, J. M.; Fernández, J. J.; Fernández, A.; López-Torres, M.; Adams, H. *Organometallics* **1999**, *18*, 5484.
123. Wilkins, R. G. *Kinetics and Mechanism of Reactions of Transition Metals*, 2nd ed.; VCH: Weinheim, 1991; Chapter 4.
124. (a) Grim, S. O.; Barth, R.; Mitchell, J. and DelGaudio, J. *Inorg. Chem.*, **1977**, *16*, 1776. (b) Grim, S. O.; Briggs, W.; Barth, R.; Tolman, C. A. and Jesson, J. P. *Inorg. Chem.*, **1974**, *13*, 1095.
125. Tau, K. D.; Uriarte, R. Mazanec, T. J. and Meek, D. W. *J. Am. Chem. Soc.*, **1979**, *101*, 6614.
126. Gottfried, H. B. *J. Am. Chem. Soc.*, **1932**, *54*, 748.
127. Parshall, G. W. *J. Inorg. Nuclear Chem.*, **1960**, *14*, 291.
128. Ellermann, J.; Schirmacher, D. *Chem. Ber.*, **1967**, *100*, 2220.
129. Grim, S. O.; Mitchell, J. D. *J. Chem. Soc., Chem. Commun.* **1975**, 634.
130. Berlin, K. D.; Hopper, D. G. *Proc. Okla. Acad. Sci.*, **1966**, *46*, 85.
131. Brown, D. H.; Gross, R. J.; Keat, R. *J. Chem. Soc., Chem. Commun.* **1977**, 708.
132. Mann, F. G.; Millar, I. T. *J. Chem. Soc.* **1952**, 4453.
133. Hoff, M. C.; Hill, P. *J. Org. Chem.* **1959**, *24*, 356.
134. Rauhut, M. M.; Hechenbleikner, I.; Currier, H. A.; Schaefer, F. C.; Wystrach, V. P. *J. Am. Chem. Soc.*, **1959**, *81*, 1103.

135. Rauhut, M. M.; Currier, H. A.; Semsel, A. M.; Wystrach, V. P. *J. Org. Chem.* **1961**, *26*, 5138.
136. (a) Mirzaei, F.; Han, L. B.; Tanaka, M. *Tetrahedron Lett.* **2001**, *42*, 297. (b) Han, L. B.; Zhang, C.; Yazawa, H.; Shimada, S. *J. Am. Chem. Soc.*, **2004**, *126*, 5080. (c) Han, L. B.; Zhao, C. Q.; Tanaka, M. *J. Org. Chem.* **2001**, *66*, 5929.
137. Malisch, W.; Klüpfel, B.; Schumacher, D.; Nieger, M. *J. Organomet. Chem.* **2002**, *661*, 95.
138. Shaw, M. A.; Tebby, J. C. *J. Chem. Soc. (C)* **1970**, 5.
139. (a) Malisch, W.; Rehmann, F. -J.; Jehle, H.; Reising, J. *J. Organomet. Chem.* **1998**, *570*, 107. (b) Treichel, P. M.; Wong, W. K. *J. Organomet. Chem.* **1978**, *157*, C5.

PUBLICATIONS

Lulu Tang, Yi Zhang, Luo Ding, Yongxin Li, Kum-Fun Mok, Wee-Chuan Yeo and Pak-Hing Leung.

Asymmetric synthesis of dimethyl-1,2-bis-(diphenylphosphino)-1,2-ethanedicarboxylate by means of a chiral palladium(II) template promoted hydrophosphination reaction *Tetrahedron Letters* **2007**, 48, 33.

Wee-Chuan Yeo, Lulu Tang, Bin Yan, Si-Yin Tee, Lip Lin Koh, Geok-Kheng Tan and Pak-Hing Leung.

Chiral metal template induced asymmetric synthesis of a mixed phosphine-phosphine oxide ligand *Organometallics* **2005**, 24, 5581.

APPENDIX

Table A 1 Crystallographic Data for Dichloro Complex **138**

Empirical formula	C ₃₈ H ₃₃ Cl ₂ O P ₃ Pd
Formula weight	775.85
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 22.2073(6) Å α = 90°. b = 17.5926(5) Å β = 96.5090(10)°. c = 18.0160(4) Å γ = 90°.
Volume	6993.2(3) Å ³
Z	8
Density (calculated)	1.474 Mg/m ³
Absorption coefficient	0.851 mm ⁻¹
F(000)	3152
Crystal size	0.05 x 0.05 x 0.03 mm ³
Theta range for data collection	1.80 to 28.29°.
Index ranges	-29 ≤ h ≤ 29, -23 ≤ k ≤ 23, -23 ≤ l ≤ 24
Reflections collected	78051
Independent reflections	17320 [R(int) = 0.0438]
Completeness to theta = 28.29°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9749 and 0.9587
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	17320 / 0 / 811
Goodness-of-fit on F ²	1.102
Final R indices [I > 2σ(I)]	R ₁ = 0.0468, wR ₂ = 0.1083
R indices (all data)	R ₁ = 0.0721, wR ₂ = 0.1224
Largest diff. peak and hole	2.482 and -1.347 e.Å ⁻³

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b wR_2 = \sqrt{\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}}, w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP.$$

Table A 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex **138**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	3136(1)	7277(1)	11258(1)	22(1)
Pd(2)	1946(1)	3101(1)	3642(1)	37(1)
Cl(1)	3366(1)	6710(1)	12442(1)	34(1)
Cl(2)	2363(1)	8061(1)	11641(1)	38(1)
Cl(3)	1635(1)	3677(1)	4710(1)	79(1)
Cl(4)	2838(1)	2599(1)	4280(1)	75(1)
O(1)	4784(1)	5939(2)	9318(1)	31(1)
O(2)	158(1)	3819(2)	1212(2)	45(1)
P(1)	3029(1)	7631(1)	10061(1)	23(1)
P(2)	3749(1)	6525(1)	10688(1)	21(1)
P(3)	4496(1)	6555(1)	8839(1)	23(1)
P(4)	1220(1)	3622(1)	2835(1)	32(1)
P(5)	2085(1)	2624(1)	2534(1)	32(1)
P(6)	515(1)	3268(1)	811(1)	34(1)
C(1)	2359(2)	7237(2)	9538(2)	28(1)
C(2)	1929(2)	6881(3)	9919(2)	44(1)
C(3)	1430(2)	6532(3)	9523(3)	57(1)
C(4)	1361(2)	6532(3)	8762(3)	53(1)
C(5)	1772(2)	6918(3)	8376(2)	46(1)
C(6)	2272(2)	7268(2)	8757(2)	33(1)
C(7)	3106(2)	8620(2)	9799(2)	27(1)
C(8)	2708(2)	9150(3)	10054(2)	42(1)
C(9)	2769(2)	9912(3)	9897(3)	50(1)
C(10)	3210(2)	10151(3)	9474(3)	50(1)
C(11)	3599(2)	9633(3)	9213(3)	49(1)
C(12)	3553(2)	8863(2)	9376(2)	37(1)
C(13)	3715(2)	7125(2)	9826(2)	21(1)
C(14)	3737(2)	6810(2)	9037(2)	24(1)
C(15)	4416(2)	6316(2)	7854(2)	27(1)
C(16)	3863(2)	6216(2)	7427(2)	33(1)

C(17)	3840(2)	5951(3)	6698(2)	43(1)
C(18)	4364(2)	5806(2)	6386(2)	45(1)
C(19)	4914(2)	5903(3)	6800(2)	49(1)
C(20)	4943(2)	6163(3)	7532(2)	39(1)
C(21)	4920(2)	7428(2)	8972(2)	27(1)
C(22)	4846(2)	8035(2)	8470(2)	35(1)
C(23)	5164(2)	8703(3)	8624(3)	46(1)
C(24)	5556(2)	8769(3)	9275(3)	56(1)
C(25)	5633(2)	8172(3)	9774(3)	50(1)
C(26)	5318(2)	7498(2)	9624(2)	36(1)
C(27)	4525(2)	6440(2)	11105(2)	24(1)
C(28)	4805(2)	7102(2)	11385(2)	34(1)
C(29)	5400(2)	7088(3)	11718(2)	42(1)
C(30)	5705(2)	6399(3)	11789(2)	43(1)
C(31)	5426(2)	5739(3)	11522(3)	44(1)
C(32)	4838(2)	5756(2)	11176(2)	34(1)
C(33)	3399(2)	5618(2)	10428(2)	27(1)
C(34)	3643(2)	5119(2)	9940(2)	34(1)
C(35)	3312(2)	4475(2)	9697(2)	44(1)
C(36)	2752(2)	4339(3)	9923(3)	51(1)
C(37)	2516(2)	4821(3)	10413(3)	50(1)
C(38)	2839(2)	5460(2)	10672(2)	39(1)
C(39)	438(2)	3606(3)	3020(2)	38(1)
C(40)	179(2)	2911(3)	3191(3)	55(1)
C(41)	-416(3)	2899(4)	3349(3)	72(2)
C(42)	-751(2)	3558(4)	3353(3)	67(2)
C(43)	-498(2)	4232(4)	3184(3)	66(2)
C(44)	96(2)	4262(3)	3006(3)	50(1)
C(45)	1421(2)	4582(2)	2599(2)	34(1)
C(46)	1839(2)	4971(3)	3089(3)	44(1)
C(47)	2022(2)	5700(3)	2928(3)	51(1)
C(48)	1791(2)	6049(3)	2282(3)	48(1)
C(49)	1367(2)	5673(3)	1793(3)	48(1)
C(50)	1178(2)	4943(3)	1947(3)	44(1)
C(51)	1337(2)	2947(2)	2064(2)	33(1)
C(52)	1293(2)	3154(2)	1248(2)	34(1)
C(53)	638(2)	3590(3)	-115(2)	41(1)
C(54)	262(3)	4145(4)	-438(3)	71(2)
C(55)	389(3)	4491(4)	-1101(4)	88(2)

C(56)	872(3)	4262(4)	-1449(3)	68(2)
C(57)	1248(3)	3710(3)	-1122(3)	57(1)
C(58)	1134(2)	3373(3)	-464(3)	50(1)
C(59)	171(2)	2335(3)	777(2)	39(1)
C(60)	268(2)	1801(3)	247(3)	53(1)
C(61)	-29(3)	1104(3)	250(3)	66(2)
C(62)	-418(3)	943(3)	754(3)	73(2)
C(63)	-501(3)	1468(3)	1301(4)	76(2)
C(64)	-220(2)	2164(3)	1307(3)	57(1)
C(65)	2138(2)	1611(2)	2373(2)	38(1)
C(66)	1796(2)	1252(3)	1777(2)	45(1)
C(67)	1882(2)	479(3)	1662(3)	54(1)
C(68)	2282(3)	72(3)	2132(3)	64(2)
C(69)	2609(3)	418(3)	2719(4)	73(2)
C(70)	2547(2)	1194(3)	2845(3)	56(1)
C(71)	2687(2)	3062(2)	2094(2)	36(1)
C(72)	2895(2)	2745(3)	1468(3)	49(1)
C(73)	3353(2)	3091(3)	1139(3)	56(1)
C(74)	3606(2)	3758(4)	1429(3)	60(2)
C(75)	3409(2)	4082(3)	2054(3)	56(1)
C(76)	2948(2)	3730(3)	2404(3)	45(1)

Table A 3 Crystallographic Data for Dichloro Complex (S)-**141**

Empirical formula	C ₃₈ H ₃₃ Cl ₂ O P ₃ Pd	
Formula weight	775.85	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 8.2326(8) Å	α = 90°.
	b = 20.152(2) Å	β = 90°.
	c = 20.929(2) Å	γ = 90°.
Volume	3472.3(6) Å ³	
Z	4	
Density (calculated)	1.484 Mg/m ³	
Absorption coefficient	0.857 mm ⁻¹	
F(000)	1576	
Crystal size	0.30 x 0.12 x 0.08 mm ³	
Theta range for data collection	1.40 to 27.49°.	
Index ranges	-10 ≤ h ≤ 10, -26 ≤ k ≤ 20, -25 ≤ l ≤ 27	
Reflections collected	24772	
Independent reflections	7982 [R(int) = 0.0440]	
Completeness to theta = 27.49°	100.0 %	
Absorption correction	Sadabs, (Sheldrick 2001)	
Max. and min. transmission	0.9346 and 0.7832	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7982 / 0 / 376	
Goodness-of-fit on F ²	1.067	
Final R indices [I > 2σ(I)]	R ₁ = 0.0479, wR ₂ = 0.0995	
R indices (all data)	R ₁ = 0.0564, wR ₂ = 0.1032	
Absolute structure parameter	0.01(3)	
Largest diff. peak and hole	0.886 and -0.317 e.Å ⁻³	

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$

^b $wR_2 = \sqrt{\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}}, w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$

Table A 4 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex (*S*)-**141**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	2667(1)	9346(1)	4046(1)	36(1)
Cl(1)	901(2)	9014(1)	3225(1)	61(1)
Cl(2)	500(1)	9381(1)	4786(1)	64(1)
P(1)	4854(1)	9251(1)	3415(1)	37(1)
P(2)	4463(1)	9603(1)	4807(1)	37(1)
P(3)	6158(1)	10798(1)	4175(1)	40(1)
O(1)	4582(3)	10939(2)	3859(2)	51(1)
C(1)	6703(5)	9460(2)	3872(2)	40(1)
C(2)	6349(4)	9931(2)	4422(2)	35(1)
C(3)*	5121(8)	8398(2)	3147(3)	46(4)
C(4)*	5739(8)	7922(3)	3561(2)	66(2)
C(5)*	5959(7)	7274(3)	3352(3)	79(3)
C(6)*	5561(8)	7102(2)	2728(3)	62(2)
C(7)*	4944(8)	7578(3)	2313(2)	71(3)
C(8)*	4724(8)	8226(3)	2523(3)	63(2)
C(3A)#	5298(12)	8430(4)	3102(4)	41(6)
C(4A)#	6874(10)	8190(4)	3049(4)	70(4)
C(5A)#	7172(9)	7605(5)	2717(5)	82(4)
C(6A)#	5893(12)	7261(4)	2437(4)	65(4)
C(7A)#	4316(10)	7502(4)	2489(4)	79(5)
C(8A)#	4019(9)	8087(5)	2822(4)	63(4)
C(9)	4883(6)	9741(2)	2687(2)	43(1)
C(10)	6219(7)	9684(3)	2285(3)	84(2)
C(11)	6194(10)	10020(4)	1707(3)	95(2)
C(12)	4935(9)	10406(3)	1538(3)	79(2)
C(13)	3657(8)	10452(3)	1922(3)	67(2)
C(14)	3608(6)	10118(3)	2504(2)	51(1)
C(15)	5110(6)	8845(2)	5210(2)	46(1)
C(16)	4004(8)	8355(3)	5311(3)	79(2)
C(17)	4449(11)	7773(4)	5598(4)	109(3)

C(18)	5991(10)	7680(4)	5806(3)	90(2)
C(19)	7111(9)	8152(3)	5714(3)	86(2)
C(20)	6688(7)	8738(3)	5409(3)	63(1)
C(21)	3907(6)	10191(2)	5431(2)	45(1)
C(22)	4568(6)	10146(3)	6032(2)	66(2)
C(23)	4263(9)	10618(4)	6482(3)	89(2)
C(24)	3306(10)	11141(4)	6343(3)	94(2)
C(25)	2564(8)	11182(3)	5749(3)	89(2)
C(26)	2863(6)	10707(3)	5292(3)	66(1)
C(27)	6536(6)	11318(2)	4863(2)	47(1)
C(28)	7666(7)	11177(3)	5340(2)	60(1)
C(29)	7906(8)	11623(3)	5838(3)	78(2)
C(30)	7027(9)	12203(3)	5856(3)	85(2)
C(31)	5924(9)	12345(3)	5390(4)	87(2)
C(32)	5668(7)	11906(3)	4894(3)	69(2)
C(33)	7852(5)	10951(2)	3657(2)	44(1)
C(34)	9452(6)	10921(3)	3846(2)	53(1)
C(35)	10680(6)	11087(3)	3445(3)	69(2)
C(36)	10338(8)	11278(4)	2835(4)	99(2)
C(37)	8751(9)	11279(5)	2604(4)	116(3)
C(38)	7521(7)	11111(3)	3025(3)	77(2)

*sof = 0.6 #sof=0.4

Table A 5 Crystallographic Data for Complex (S,S)-**144a**

Empirical formula	C52.50 H49.75 Cl N1.25 O4 P3 Pd S
Formula weight	1029.01
Temperature	223(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)
Unit cell dimensions	a = 11.5306(4) Å α = 90°. b = 29.7758(13) Å β = 95.238(2)°. c = 15.9042(6) Å γ = 90°.
Volume	5437.6(4) Å ³
Z	4
Density (calculated)	1.257 Mg/m ³
Absorption coefficient	0.558 mm ⁻¹
F(000)	2118
Crystal size	0.30 x 0.20 x 0.20 mm ³
Theta range for data collection	2.20 to 27.85°.
Index ranges	-14 ≤ h ≤ 15, -39 ≤ k ≤ 34, -20 ≤ l ≤ 20
Reflections collected	55618
Independent reflections	23486 [R(int) = 0.0428]
Completeness to theta = 27.85°	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8965 and 0.8504
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	23486 / 5 / 1169
Goodness-of-fit on F ²	1.154
Final R indices [I > 2σ(I)]	R1 = 0.0873, wR2 = 0.2218
R indices (all data)	R1 = 0.0967, wR2 = 0.2274
Absolute structure parameter	0.08(4)
Largest diff. peak and hole	1.488 and -2.504 e.Å ⁻³

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b wR_2 = \sqrt{\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}}, w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP.$$

Table A 6 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex (S,S)-**144a**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	6830(1)	3712(1)	758(1)	30(1)
Pd(2)	654(1)	2304(1)	6367(1)	31(1)
Cl(1)	9558(3)	5230(1)	1873(3)	65(1)
Cl(2)	6992(6)	1883(2)	3540(3)	112(2)
N(1)	7073(7)	3299(3)	1877(5)	33(2)
N(2)	438(7)	1590(3)	6472(4)	34(2)
N(3)	3780(20)	2542(9)	9190(20)	97(10)
O(1)	9501(8)	4751(3)	1860(6)	63(2)
O(2)	8502(11)	5403(4)	1482(10)	102(4)
O(3)	9678(13)	5400(4)	2717(9)	111(5)
O(4)	10479(12)	5378(5)	1451(12)	140(7)
O(5)	7218(13)	1733(6)	2740(9)	126(6)
O(6)	7582(15)	1705(8)	4223(10)	172(9)
O(7)	7360(50)	2310(10)	3503(15)	360(30)
O(8)	5900(30)	1920(20)	3683(14)	450(40)
P(1)	5420(2)	4222(1)	1202(1)	28(1)
P(2)	6692(2)	4094(1)	-466(2)	31(1)
P(3)	4426(2)	5168(1)	347(2)	37(1)
P(4)	2076(2)	2334(1)	5361(1)	30(1)
P(5)	702(2)	3051(1)	6330(1)	27(1)
P(6)	2956(2)	3189(1)	4267(2)	33(1)
S(1)	2888(2)	5005(1)	-163(2)	51(1)
S(2)	4541(2)	3270(1)	4777(2)	47(1)
C(1)	8064(7)	3260(4)	379(6)	34(2)
C(2)	8815(8)	3333(4)	-281(6)	38(2)
C(3)	9607(9)	3000(4)	-394(6)	45(3)
C(4)	9713(8)	2605(4)	45(6)	41(2)
C(5)	10491(10)	2247(6)	-115(8)	64(4)
C(6)	10491(13)	1850(5)	313(8)	68(4)
C(7)	9708(15)	1781(5)	947(9)	79(5)

C(8)	8980(11)	2126(4)	1132(7)	54(3)
C(9)	8942(9)	2526(4)	699(7)	43(3)
C(10)	8139(9)	2873(4)	843(7)	44(2)
C(11)	7314(11)	2825(4)	1504(6)	46(3)
C(12)	6183(10)	2613(4)	1171(8)	54(3)
C(13)	6149(10)	3285(4)	2464(7)	49(3)
C(14)	8171(10)	3459(4)	2372(6)	51(3)
C(15)	5427(8)	4475(4)	-455(6)	38(2)
C(16)	5452(7)	4685(3)	426(6)	32(2)
C(17)	3928(8)	3999(4)	1172(7)	41(2)
C(18)	3746(8)	3582(3)	846(6)	37(2)
C(19)	2622(10)	3387(5)	802(8)	54(3)
C(20)	1721(8)	3623(5)	1098(7)	52(3)
C(21)	1893(9)	4047(5)	1397(9)	58(3)
C(22)	2995(9)	4243(4)	1464(7)	44(2)
C(23)	5806(10)	4472(4)	2266(7)	45(2)
C(24)	5103(11)	4447(5)	2925(8)	57(3)
C(25)	5533(13)	4620(5)	3722(9)	68(4)
C(26)	6639(13)	4793(5)	3823(8)	67(4)
C(27)	7331(13)	4792(5)	3158(9)	66(4)
C(28)	6941(10)	4625(4)	2418(7)	46(2)
C(29)	6372(7)	3781(3)	-1437(5)	32(2)
C(30)	6946(11)	3836(4)	-2145(7)	52(3)
C(31)	6594(13)	3600(5)	-2906(7)	63(4)
C(32)	5680(13)	3290(6)	-2889(9)	74(5)
C(33)	5143(10)	3223(5)	-2197(8)	56(3)
C(34)	5469(8)	3463(4)	-1448(7)	46(3)
C(35)	7872(8)	4478(4)	-639(6)	37(2)
C(36)	8883(8)	4480(4)	-59(7)	46(3)
C(37)	9752(11)	4786(5)	-187(10)	66(4)
C(38)	9687(11)	5070(5)	-841(10)	63(3)
C(39)	8717(12)	5077(4)	-1417(9)	62(3)
C(40)	7760(11)	4787(4)	-1296(9)	57(3)
C(41)	4413(10)	5421(4)	1385(8)	51(3)
C(42)	3424(12)	5457(4)	1770(8)	58(3)
C(43)	3381(16)	5643(5)	2570(8)	73(5)
C(44)	4420(20)	5810(5)	2962(9)	87(6)
C(45)	5389(17)	5760(6)	2645(12)	87(5)
C(46)	5475(12)	5582(5)	1812(8)	60(3)

C(47)	5172(11)	5565(4)	-315(8)	53(3)
C(48)	6395(12)	5633(5)	-239(11)	75(5)
C(49)	6850(20)	5926(6)	-778(15)	107(7)
C(50)	6180(20)	6143(7)	-1377(17)	122(9)
C(51)	5060(30)	6087(6)	-1426(12)	112(8)
C(52)	4509(15)	5804(4)	-912(8)	64(4)
C(53)	-567(7)	2297(4)	7236(5)	33(2)
C(54)	-1328(8)	2653(4)	7450(6)	39(2)
C(55)	-2121(9)	2572(4)	8022(6)	44(3)
C(56)	-2170(8)	2156(4)	8442(6)	41(3)
C(57)	-2976(9)	2076(5)	9067(6)	50(3)
C(58)	-3021(13)	1682(5)	9475(9)	67(4)
C(59)	-2269(13)	1331(5)	9277(9)	65(4)
C(60)	-1563(11)	1392(4)	8667(8)	51(3)
C(61)	-1445(8)	1800(4)	8235(6)	38(2)
C(62)	-647(8)	1875(4)	7625(6)	39(2)
C(63)	176(11)	1517(4)	7387(6)	43(2)
C(64)	1284(10)	1519(5)	7973(7)	54(3)
C(65)	1373(13)	1301(4)	6228(8)	58(3)
C(66)	-612(12)	1465(4)	5910(8)	55(3)
C(67)	1953(7)	3224(3)	5774(5)	31(2)
C(68)	1978(7)	2928(3)	4989(5)	29(2)
C(69)	3558(8)	2220(3)	5816(6)	34(2)
C(70)	3719(9)	2167(4)	6691(6)	43(2)
C(71)	4842(10)	2076(4)	7086(6)	49(3)
C(72)	5738(10)	2028(4)	6606(8)	54(3)
C(73)	5579(9)	2072(5)	5723(7)	51(3)
C(74)	4503(9)	2192(4)	5333(7)	52(3)
C(75)	1771(8)	1964(4)	4437(6)	36(2)
C(76)	2500(11)	1643(5)	4217(9)	60(3)
C(77)	2151(15)	1341(5)	3582(9)	69(4)
C(78)	1092(17)	1355(6)	3202(11)	83(5)
C(79)	313(12)	1686(5)	3392(9)	66(4)
C(80)	638(11)	1990(5)	4020(7)	53(3)
C(81)	933(8)	3383(3)	7309(6)	33(2)
C(82)	1874(9)	3264(4)	7845(6)	46(3)
C(83)	2139(10)	3509(5)	8557(7)	58(3)
C(84)	1499(11)	3884(5)	8734(8)	63(4)
C(85)	545(13)	3995(5)	8200(7)	61(4)

C(86)	183(10)	3741(5)	7465(10)	72(4)
C(87)	-534(8)	3297(4)	5687(6)	36(2)
C(88)	-1447(8)	3000(4)	5383(6)	42(2)
C(89)	-2370(8)	3201(5)	4866(6)	47(3)
C(90)	-2430(9)	3626(6)	4687(7)	61(4)
C(91)	-1526(10)	3914(4)	4968(8)	54(3)
C(92)	-566(9)	3740(5)	5470(7)	50(3)
C(93)	2838(8)	2851(4)	3339(7)	41(2)
C(94)	3802(9)	2613(4)	3127(7)	49(3)
C(95)	3714(10)	2322(5)	2424(8)	57(3)
C(96)	2703(13)	2288(5)	1937(7)	65(3)
C(97)	1743(12)	2527(5)	2123(8)	69(4)
C(98)	1813(9)	2797(5)	2808(8)	62(4)
C(99)	2242(9)	3731(4)	4036(6)	44(2)
C(100)	2826(14)	4082(6)	4179(15)	97(6)
C(101)	2340(30)	4512(8)	4060(20)	167(14)
C(102)	1219(19)	4556(6)	3686(13)	95(6)
C(103)	574(14)	4181(6)	3552(10)	75(4)
C(104)	1102(13)	3772(6)	3666(10)	81(5)
C(105)	3860(20)	2162(9)	9375(17)	62(6)
C(106)	3930(30)	1691(9)	9390(30)	117(16)

Table A 7 Crystallographic Data for Complex (S,S,Sp)-**152a**

Empirical formula	C ₄₈ H ₄₉ Cl N O ₅ P ₃ Pd
Formula weight	954.64
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 10.8799(10) Å α = 90°. b = 19.1760(18) Å β = 90°. c = 21.649(2) Å γ = 90°.
Volume	4516.7(8) Å ³
Z	4
Density (calculated)	1.404 Mg/m ³
Absorption coefficient	0.623 mm ⁻¹
F(000)	1968
Crystal size	0.20 x 0.14 x 0.08 mm ³
Theta range for data collection	1.42 to 27.50°.
Index ranges	-12 ≤ h ≤ 14, -22 ≤ k ≤ 24, -28 ≤ l ≤ 23
Reflections collected	32265
Independent reflections	10356 [R(int) = 0.0680]
Completeness to theta = 27.50°	99.9 %
Absorption correction	Sadabs, (Sheldrick 2001)
Max. and min. transmission	0.9519 and 0.8856
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	10356 / 0 / 532
Goodness-of-fit on F ²	1.035
Final R indices [I > 2σ(I)]	R ₁ = 0.0619, wR ₂ = 0.1122
R indices (all data)	R ₁ = 0.0859, wR ₂ = 0.1206
Absolute structure parameter	-0.01(3)
Largest diff. peak and hole	0.915 and -0.404 e.Å ⁻³

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b wR_2 = \sqrt{\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}}, w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP.$$

Table A 8 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex (S,S,Sp)-**152a**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	6415(1)	5666(1)	6877(1)	39(1)
P(1)	7540(1)	4857(1)	7361(1)	38(1)
P(2)	7242(1)	5191(1)	5956(1)	40(1)
P(3)	9726(1)	4302(1)	5714(1)	46(1)
O(1)	9156(3)	3766(2)	5329(2)	56(1)
N(1)	5208(4)	6446(2)	6500(2)	52(1)
C(1)	4694(5)	6489(3)	7589(3)	46(1)
C(2)	5786(5)	6110(3)	7677(3)	43(1)
C(3)	6293(5)	6111(3)	8275(2)	48(1)
C(4)	5782(5)	6474(3)	8753(3)	54(2)
C(5)	4665(5)	6835(3)	8674(3)	52(2)
C(6)	4092(6)	7174(3)	9176(3)	64(2)
C(7)	3002(6)	7503(3)	9104(4)	71(2)
C(8)	2451(6)	7511(3)	8520(4)	68(2)
C(9)	2980(5)	7200(3)	8021(3)	57(2)
C(10)	4117(4)	6842(2)	8094(3)	48(1)
C(11)	4164(5)	6488(3)	6948(3)	60(2)
C(12)	3275(5)	5884(3)	6882(3)	74(2)
C(13)	5898(6)	7125(3)	6506(3)	71(2)
C(14)	4757(7)	6340(4)	5866(3)	78(2)
C(15)	5560(6)	3994(4)	7637(3)	84(2)
C(16)	6754(4)	4266(3)	7887(3)	52(1)
C(17)	8873(4)	5189(3)	7766(2)	42(1)
C(18)	9580(5)	4752(3)	8136(3)	61(2)
C(19)	10615(6)	4999(4)	8436(3)	77(2)
C(20)	10958(6)	5680(5)	8361(3)	76(2)
C(21)	10279(5)	6116(4)	7988(4)	75(2)
C(22)	9248(5)	5863(3)	7689(3)	53(2)
C(23)	8211(4)	4292(3)	6776(2)	45(1)
C(24)	8666(5)	4762(2)	6231(2)	41(1)

C(25)	10851(5)	3924(3)	6226(3)	52(2)
C(26)	11147(6)	3219(3)	6137(3)	72(2)
C(27)	11990(8)	2906(5)	6522(5)	100(3)
C(28)	12526(7)	3265(5)	6984(5)	103(3)
C(29)	12249(6)	3958(5)	7077(4)	87(2)
C(30)	11420(5)	4284(4)	6703(3)	70(2)
C(31)	10514(5)	4968(3)	5270(3)	52(2)
C(32)	10969(5)	5588(4)	5523(3)	76(2)
C(33)	11565(7)	6053(4)	5143(4)	95(3)
C(34)	11705(7)	5929(5)	4530(5)	107(3)
C(35)	11245(9)	5340(5)	4283(4)	106(3)
C(36)	10642(7)	4853(4)	4645(3)	84(2)
C(37)	6284(5)	4548(2)	5577(2)	45(1)
C(38)	6580(6)	4229(3)	5019(3)	59(2)
C(39)	5749(7)	3791(4)	4730(3)	73(2)
C(40)	4638(8)	3668(4)	4989(4)	85(2)
C(41)	4338(6)	3957(4)	5532(4)	83(2)
C(42)	5150(5)	4399(3)	5832(3)	61(2)
C(43)	7639(5)	5838(3)	5376(3)	53(1)
C(44)	8371(6)	6392(3)	5561(3)	72(2)
C(45)	8568(9)	6949(4)	5149(5)	105(3)
C(46)	8005(9)	6936(5)	4594(4)	103(3)
C(47)	7265(8)	6416(4)	4416(3)	86(2)
C(48)	7089(6)	5859(3)	4799(3)	69(2)
Cl(1)	4917(3)	2361(1)	1720(1)	120(1)
O(2)	4185(8)	2859(4)	1462(4)	184(4)
O(3)	5332(7)	1868(3)	1291(3)	147(3)
O(4)	4307(7)	2015(3)	2201(4)	152(3)
O(5)	5971(7)	2707(3)	1961(4)	163(3)

Table A 9 Crystallographic Data for Dichloro Complex **161**

Empirical formula	C ₃₃ H ₃₁ Cl ₂ NOP ₂ Pd 0.25 {CH ₂ Cl ₂ }.0.5 {H ₂ O}	
Formula weight	727.07	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 27.5531(19) Å	α = 90°.
	b = 12.0672(8) Å	β = 107.096(2)°.
	c = 41.462(3) Å	γ = 90°.
Volume	13176.5(15) Å ³	
Z	16	
Density (calculated)	1.466 Mg/m ³	
Absorption coefficient	0.892 mm ⁻¹	
F(000)	5912	
Crystal size	0.20 x 0.10 x 0.08 mm ³	
Theta range for data collection	1.03 to 25.00°.	
Index ranges	-32 ≤ h ≤ 32, -14 ≤ k ≤ 14, -49 ≤ l ≤ 39	
Reflections collected	37885	
Independent reflections	11605 [R(int) = 0.0781]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Sadabs, (Sheldrick 2001)	
Max. and min. transmission	0.9321 and 0.8418	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	11605 / 10 / 752	
Goodness-of-fit on F ²	1.060	
Final R indices [I > 2σ(I)]	R ₁ = 0.0686, wR ₂ = 0.1284	
R indices (all data)	R ₁ = 0.1115, wR ₂ = 0.1423	
Largest diff. peak and hole	0.838 and -0.825 e.Å ⁻³	

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b wR_2 = \sqrt{\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}}, w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP.$$

Table A 10 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex **161**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	1607(1)	3401(1)	1273(1)	43(1)
Pd(2)	1631(1)	6758(1)	958(1)	38(1)
Cl(1)	2408(1)	2856(2)	1566(1)	76(1)
Cl(2)	1831(1)	3682(1)	762(1)	60(1)
Cl(3)	1690(1)	7233(2)	1505(1)	65(1)
Cl(4)	747(1)	6413(1)	842(1)	52(1)
P(1)	1381(1)	3344(1)	1742(1)	41(1)
P(2)	480(1)	4813(1)	1886(1)	43(1)
P(3)	2443(1)	7073(1)	1033(1)	39(1)
P(4)	3146(1)	6240(1)	577(1)	41(1)
O(1)	192(2)	3886(3)	1980(1)	52(1)
O(2)	3124(2)	7123(3)	326(1)	52(1)
N(1)	859(2)	3853(4)	1039(1)	41(1)
N(2)	1615(2)	6223(4)	477(1)	36(1)
C(1)	860(2)	4381(4)	1613(2)	38(2)
C(2)	539(2)	3960(5)	1266(2)	40(2)
C(3)	588(3)	3245(5)	718(2)	57(2)
C(4)	560(3)	2003(6)	759(2)	62(2)
C(5)	127(4)	1502(8)	787(3)	100(3)
C(6)	99(5)	350(9)	810(3)	138(5)
C(7)	499(6)	-284(8)	801(3)	136(5)
C(8)	928(4)	197(7)	771(3)	100(3)
C(9)	963(3)	1333(6)	754(2)	71(2)
C(10)	1838(2)	3751(5)	2132(2)	45(2)
C(11)	1978(3)	3051(6)	2406(2)	62(2)
C(12)	2341(3)	3356(8)	2697(2)	75(2)
C(13)	2578(3)	4335(10)	2719(2)	90(3)
C(14)	2441(4)	5055(8)	2447(3)	91(3)
C(15)	2077(3)	4757(6)	2150(2)	70(2)
C(16)	1135(3)	1999(5)	1811(2)	46(2)

C(17)	856(3)	1825(5)	2034(2)	53(2)
C(18)	688(3)	770(6)	2080(2)	66(2)
C(19)	819(4)	-102(7)	1910(2)	84(3)
C(20)	1102(4)	39(6)	1691(2)	84(3)
C(21)	1258(3)	1101(6)	1641(2)	68(2)
C(22)	905(3)	5478(5)	2245(2)	51(2)
C(23)	997(3)	4970(7)	2553(2)	72(2)
C(24)	1332(4)	5424(9)	2840(2)	89(3)
C(25)	1560(4)	6390(11)	2821(3)	108(4)
C(26)	1468(4)	6952(9)	2522(3)	103(4)
C(27)	1139(3)	6483(7)	2226(2)	83(3)
C(28)	53(3)	5861(5)	1657(2)	49(2)
C(29)	201(3)	6741(6)	1491(2)	74(2)
C(30)	-155(5)	7539(8)	1331(2)	95(3)
C(31)	-641(5)	7455(8)	1328(3)	102(4)
C(32)	-801(4)	6584(9)	1477(3)	102(3)
C(33)	-451(3)	5776(6)	1647(2)	69(2)
C(34)	2557(2)	6169(5)	702(2)	35(2)
C(35)	2109(2)	6275(5)	391(2)	41(2)
C(36)	1189(2)	6608(5)	187(2)	49(2)
C(37)	997(2)	5709(6)	-67(2)	48(2)
C(38)	1176(3)	5579(7)	-342(2)	78(3)
C(39)	994(4)	4745(9)	-574(2)	101(3)
C(40)	633(4)	4028(8)	-524(2)	87(3)
C(41)	463(3)	4111(8)	-252(2)	84(3)
C(42)	641(3)	4963(6)	-27(2)	60(2)
C(43)	2526(2)	8527(5)	962(2)	51(2)
C(44)	2438(3)	9245(6)	1206(2)	75(3)
C(45)	2450(4)	10368(7)	1153(3)	99(3)
C(46)	2535(4)	10793(7)	875(3)	111(4)
C(47)	2616(4)	10089(7)	636(3)	102(3)
C(48)	2611(3)	8954(5)	677(2)	69(2)
C(49)	2890(2)	6673(6)	1429(2)	47(2)
C(50)	3263(3)	7357(7)	1618(2)	65(2)
C(51)	3591(3)	6959(9)	1923(2)	85(3)
C(52)	3532(4)	5917(10)	2027(2)	97(3)
C(53)	3167(4)	5236(9)	1848(2)	93(3)
C(54)	2835(3)	5616(7)	1546(2)	69(2)
C(55)	3671(2)	6418(5)	948(2)	48(2)

C(56)	3875(3)	7462(6)	1018(2)	64(2)
C(57)	4282(4)	7657(8)	1297(3)	83(3)
C(58)	4491(3)	6806(10)	1502(3)	92(3)
C(59)	4303(3)	5750(9)	1443(2)	90(3)
C(60)	3885(3)	5560(6)	1162(2)	67(2)
C(61)	3208(2)	4880(5)	409(2)	46(2)
C(62)	3480(4)	4843(7)	184(2)	109(4)
C(63)	3559(5)	3841(10)	39(3)	134(5)
C(64)	3361(4)	2916(9)	114(3)	107(4)
C(65)	3098(4)	2933(8)	336(3)	123(5)
C(66)	3020(3)	3921(6)	483(3)	95(3)
O(1S)*	10000	2570(7)	2500	107(3)
O(2S)*	153(5)	8979(17)	29(5)	241(10)
Cl(1S)	4582(3)	3590(6)	2226(1)	276(3)
C(1S)*	5000	2696(13)	2500	248(18)

*sof=0.5

Table A 11 Crystallographic Data for Complex (S,Sp)-165a

Empirical formula	C ₄₈ H ₅₃ Cl N O ₇ P ₃ Pd
Formula weight	990.67
Temperature	223(2) K
Wavelength	0.71073 Å
Crystal system	Tetragonal
Space group	P4(1)2(1)2
Unit cell dimensions	a = 15.8922(3) Å α = 90°. b = 15.8922(3) Å β = 90°. c = 37.0730(13) Å γ = 90°.
Volume	9363.2(4) Å ³
Z	8
Density (calculated)	1.406 Mg/m ³
Absorption coefficient	0.607 mm ⁻¹
F(000)	4096
Crystal size	0.30 x 0.22 x 0.10 mm ³
Theta range for data collection	1.81 to 25.00°.
Index ranges	-18 ≤ h ≤ 12, -18 ≤ k ≤ 18, -44 ≤ l ≤ 43
Reflections collected	54418
Independent reflections	8234 [R(int) = 0.0737]
Completeness to theta = 25.00°	99.9 %
Absorption correction	Sadabs, (Sheldrick 2001)
Max. and min. transmission	0.9418 and 0.8390
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8234 / 12 / 568
Goodness-of-fit on F ²	1.120
Final R indices [I > 2σ(I)]	R ₁ = 0.0490, wR ₂ = 0.1079
R indices (all data)	R ₁ = 0.0573, wR ₂ = 0.1113
Absolute structure parameter	-0.01(3)
Largest diff. peak and hole	0.721 and -0.320 e.Å ⁻³

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b wR_2 = \sqrt{\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}}, w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP.$$

Table A 12 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex (S,S_P)-**165a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	5862(1)	439(1)	9532(1)	31(1)
P(1)	7025(1)	997(1)	9835(1)	34(1)
P(2)	6619(1)	681(1)	9037(1)	35(1)
P(3)	4988(1)	2584(1)	8531(1)	56(1)
O(1)	5276(3)	2517(3)	8150(1)	77(1)
N(1)	5045(3)	126(3)	9966(1)	41(1)
C(1)	4878(3)	-63(3)	9247(2)	39(1)
C(2)	4865(3)	-387(4)	8890(2)	50(1)
C(3)	4135(4)	-668(3)	8732(2)	62(2)
C(4)	3381(4)	-646(3)	8921(2)	64(2)
C(5)	2597(5)	-902(4)	8758(3)	83(3)
C(6)	1873(5)	-863(5)	8934(3)	99(3)
C(7)	1845(4)	-565(5)	9288(3)	92(3)
C(8)	2569(3)	-295(4)	9462(2)	69(2)
C(9)	3358(3)	-345(4)	9282(2)	57(2)
C(10)	4149(3)	-69(3)	9439(2)	47(1)
C(11)	4162(3)	266(4)	9823(2)	53(2)
C(12)	3918(4)	1182(4)	9835(2)	62(2)
C(13)	5159(4)	575(5)	10312(2)	65(2)
C(14)	5171(3)	-788(4)	10039(2)	57(2)
C(15)	7907(3)	948(3)	9513(1)	41(1)
C(16)	7577(3)	1270(3)	9152(1)	40(1)
C(17)	7367(3)	419(3)	10231(1)	37(1)
C(18)	7540(4)	-435(4)	10185(2)	52(1)
C(19)	7711(4)	-940(4)	10484(2)	64(2)
C(20)	7693(4)	-580(4)	10834(2)	60(2)
C(21)	7524(4)	252(4)	10871(2)	55(2)
C(22)	7367(3)	757(3)	10576(1)	44(1)
C(23)	6994(3)	2114(3)	9950(1)	36(1)
C(24)	7687(3)	2516(3)	10100(1)	44(1)

C(25)	7670(4)	3364(4)	10166(2)	55(2)
C(26)	6969(4)	3835(4)	10072(2)	57(2)
C(27)	6274(4)	3441(4)	9922(1)	48(1)
C(28)	6287(3)	2588(3)	9862(1)	40(1)
C(29)	6093(3)	1295(4)	8686(1)	45(1)
C(30)	5704(3)	2091(4)	8846(2)	48(1)
C(31)	3982(4)	2073(4)	8590(2)	54(2)
C(32)	3546(4)	2106(4)	8910(2)	63(2)
C(33)	2761(5)	1708(5)	8940(2)	75(2)
C(34)	2448(4)	1275(4)	8651(2)	70(2)
C(35)	2878(5)	1250(4)	8331(2)	70(2)
C(36)	3636(4)	1633(4)	8302(2)	58(2)
C(37)	4880(4)	3652(4)	8684(2)	63(2)
C(38)	4843(5)	3869(4)	9040(3)	84(2)
C(39)	4746(6)	4704(5)	9150(3)	114(3)
C(40)	4694(5)	5314(5)	8888(4)	113(4)
C(41)	4721(5)	5117(6)	8531(4)	103(3)
C(42)	4827(4)	4284(4)	8424(3)	84(3)
C(43)	7018(3)	-278(3)	8829(1)	41(1)
C(44)	7404(4)	-259(5)	8496(2)	61(2)
C(45)	7730(4)	-1027(6)	8361(2)	75(2)
C(46)	7651(4)	-1761(5)	8553(2)	68(2)
C(47)	7279(4)	-1759(4)	8870(2)	62(2)
C(48)	6958(3)	-1032(4)	9011(2)	50(2)
Cl(1)	8468(2)	1532(2)	7500	135(2)
O(2)	7985(5)	1798(6)	7798(3)	205(5)
O(3)	9280(4)	1695(5)	7586(3)	197(5)
Cl(2)	6886(3)	-3114(3)	10000	170(2)
O(4)	6304(11)	-3174(14)	10258(5)	448(13)
O(5)	6796(8)	-2425(9)	9756(3)	264(7)
O(1W)*	4769(6)	5231(6)	7500	185(5)
O(2W)*	6901(7)	3346(6)	7247(3)	88(3)
O(3W)*	5338(10)	3643(8)	7594(3)	123(5)
O(4W)*	7581(11)	314(13)	11794(3)	193(9)

*sof=0.5

Table A 13 Crystallographic Data for Complex (S,Sp)-**167a**

Empirical formula	C ₄₉ H _{50.50} Cl N _{1.50} O _{4.50} P ₃ Pd S
Formula weight	999.23
Temperature	223(2) K
Wavelength	0.71073 Å
Crystal system	Tetragonal
Space group	P4(1)2(1)2
Unit cell dimensions	a = 15.9159(2) Å α = 90°. b = 15.9159(2) Å β = 90°. c = 37.5233(9) Å γ = 90°.
Volume	9505.2(3) Å ³
Z	8
Density (calculated)	1.396 Mg/m ³
Absorption coefficient	0.637 mm ⁻¹
F(000)	4120
Crystal size	0.36 x 0.16 x 0.14 mm ³
Theta range for data collection	1.81 to 25.00°
Index ranges	-16 ≤ h ≤ 18, -18 ≤ k ≤ 18, -43 ≤ l ≤ 44
Reflections collected	56559
Independent reflections	8377 [R(int) = 0.0920]
Completeness to theta = 25.00°	99.9 %
Absorption correction	Sadabs, (Sheldrick 2001)
Max. and min. transmission	0.9161 and 0.8031
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8377 / 36 / 583
Goodness-of-fit on F ²	1.089
Final R indices [I > 2σ(I)]	R ₁ = 0.0516, wR ₂ = 0.1166
R indices (all data)	R ₁ = 0.0613, wR ₂ = 0.1210
Absolute structure parameter	-0.01(3)
Largest diff. peak and hole	0.962 and -0.476 e.Å ⁻³

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b wR_2 = \sqrt{\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}}, w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP.$$

Table A 14 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex (S,S_P)-**167a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	5368(1)	9181(1)	2015(1)	26(1)
P(1)	5663(1)	8453(1)	1524(1)	30(1)
P(2)	5945(1)	8030(1)	2316(1)	31(1)
P(3)	7514(1)	10221(1)	1053(1)	34(1)
S(3)	7387(1)	9898(1)	555(1)	54(1)
N(1)	5031(3)	9990(3)	2448(1)	32(1)
C(1)	4850(3)	10891(3)	1928(1)	28(1)
C(2)	4869(3)	10160(3)	1732(2)	29(1)
C(3)	4563(4)	10178(3)	1376(2)	35(1)
C(4)	4294(4)	10917(4)	1223(2)	44(2)
C(5)	4303(4)	11665(4)	1412(2)	39(2)
C(6)	4058(4)	12442(4)	1253(2)	49(2)
C(7)	4051(4)	13170(4)	1441(2)	54(2)
C(8)	4318(4)	13178(4)	1796(2)	53(2)
C(9)	4573(4)	12449(3)	1959(2)	42(1)
C(10)	4572(4)	11669(3)	1777(2)	34(1)
C(11)	5167(3)	10864(3)	2305(2)	34(1)
C(12)	6086(4)	11120(4)	2319(2)	43(2)
C(13)	4118(4)	9853(4)	2515(2)	51(2)
C(14)	5480(5)	9873(4)	2789(2)	54(2)
C(15)	5938(4)	7164(3)	1988(2)	40(1)
C(16)	6283(4)	7524(4)	1643(2)	38(1)
C(17)	6283(4)	9015(4)	1194(1)	35(1)
C(18)	7022(4)	9482(4)	1358(2)	36(1)
C(1A)	4763(4)	8021(3)	1299(2)	40(2)
C(2A)	3980(4)	8048(4)	1461(2)	60(2)
C(3A)	3273(5)	7678(5)	1314(3)	76(3)
C(4A)	3352(7)	7292(6)	991(3)	95(4)
C(5A)	4112(8)	7274(5)	818(2)	90(3)
C(6A)	4822(5)	7639(4)	970(2)	60(2)

C(1B)	5386(4)	7663(3)	2707(2)	35(1)
C(2B)	5726(4)	7699(4)	3048(2)	42(2)
C(3B)	5241(5)	7509(4)	3339(2)	56(2)
C(4B)	4433(5)	7286(4)	3306(2)	62(2)
C(5B)	4072(5)	7232(5)	2966(3)	83(3)
C(6B)	4557(5)	7446(5)	2672(2)	57(2)
C(1C)	7056(4)	8084(4)	2421(1)	34(1)
C(2C)	7513(4)	8804(4)	2343(1)	37(1)
C(3C)	8375(4)	8828(5)	2391(2)	50(2)
C(4C)	8778(4)	8111(5)	2525(2)	53(2)
C(5C)	8333(4)	7417(5)	2615(2)	54(2)
C(6C)	7472(4)	7388(4)	2558(2)	42(2)
C(1D)	8604(4)	10256(4)	1193(2)	40(1)
C(2D)	8822(4)	10266(5)	1551(2)	55(2)
C(3D)	9656(5)	10292(6)	1647(3)	84(3)
C(4D)	10257(5)	10319(6)	1396(3)	84(3)
C(5D)	10057(5)	10302(5)	1039(3)	64(2)
C(6D)	9228(4)	10274(4)	936(2)	46(2)
C(1E)	7043(4)	11244(4)	1147(2)	39(2)
C(2E)	6556(4)	11622(4)	891(2)	54(2)
C(3E)	6201(5)	12399(5)	953(3)	68(2)
C(4E)	6347(5)	12797(5)	1269(3)	69(3)
C(5E)	6834(5)	12433(5)	1529(2)	66(2)
C(6E)	7192(5)	11655(4)	1465(2)	55(2)
Cl(1S)	6614(2)	6614(2)	0	88(1)
O(1)	6852(9)	7135(6)	272(3)	246(7)
O(2)	6786(5)	5845(5)	123(3)	149(3)
C(1S)	8686(11)	8686(11)	0	135(7)
C(2S)	9336(14)	9336(14)	0	121(8)
N(1S)	9846(10)	9846(10)	0	164(9)
O(3)	2759(11)	8078(13)	2159(7)	208(10)
O(4)	1324(12)	8030(18)	2161(14)	440(30)
O(5)	2000(20)	9180(20)	1928(9)	380(30)
O(6)	2020(30)	8940(30)	2531(6)	630(60)
Cl(2B)	2036(8)	8550(8)	2189(4)	426(18)
O(1W)	2397(9)	9741(13)	1794(3)	121(6)

Table A 15 Crystallographic Data for Complex (S,Sp)-169a

Empirical formula	C48.25 H49.50 Cl1.50 N O4 P3 Pd Se
Formula weight	1038.83
Temperature	223(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	C222(1)
Unit cell dimensions	a = 22.5184(15) Å $\alpha = 90^\circ$. b = 22.5184(15) Å $\beta = 90^\circ$. c = 37.833(4) Å $\gamma = 90^\circ$.
Volume	19185(3) Å ³
Z	16
Density (calculated)	1.439 Mg/m ³
Absorption coefficient	1.372 mm ⁻¹
F(000)	8456
Crystal size	0.40 x 0.10 x 0.10 mm ³
Theta range for data collection	1.61 to 25.00°
Index ranges	-26 ≤ h ≤ 23, -26 ≤ k ≤ 26, -44 ≤ l ≤ 44
Reflections collected	54317
Independent reflections	16697 [R(int) = 0.0927]
Completeness to theta = 25.00°	98.9 %
Absorption correction	Sadabs, (Sheldrick 2001)
Max. and min. transmission	0.8750 and 0.6098
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	16697 / 51 / 894
Goodness-of-fit on F ²	0.896
Final R indices [I > 2sigma(I)]	R1 = 0.0618, wR2 = 0.1427
R indices (all data)	R1 = 0.0902, wR2 = 0.1579
Absolute structure parameter	-0.010(17)
Largest diff. peak and hole	0.876 and -0.584 e.Å ⁻³

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b wR_2 = \sqrt{\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}}, w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP.$$

Table A 16 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex (S,S_P)-**169a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	2669(1)	6875(1)	2944(1)	33(1)
Pd(2)	8109(1)	7305(1)	4479(1)	33(1)
Se(1)	1419(1)	6063(1)	4474(1)	73(1)
P(1)	2952(1)	6424(1)	3443(1)	36(1)
P(2)	3009(1)	6010(1)	2668(1)	37(1)
P(3)	1177(1)	6233(2)	3945(1)	45(1)
P(1X)	8688(1)	7109(1)	4012(1)	36(1)
P(2X)	8938(1)	7009(1)	4814(1)	37(1)
P(3X)	8864(2)	8913(2)	3559(1)	53(1)
Se(1X)	9108(1)	8696(1)	3041(1)	79(1)
N(1)	2380(4)	7401(4)	2508(2)	37(2)
C(1)	3148(5)	5658(5)	3348(3)	40(3)
C(2)	3474(5)	5640(5)	2993(3)	42(3)
C(3)	2391(5)	6387(6)	3784(2)	42(3)
C(4)	1795(5)	6143(6)	3649(3)	50(3)
C(11)	1852(5)	7728(5)	2645(3)	46(3)
C(12)	2021(5)	7956(5)	3007(3)	43(3)
C(13)	2417(5)	7639(5)	3204(2)	40(3)
C(14)	2576(5)	7848(5)	3541(3)	52(3)
C(15)	2355(6)	8349(6)	3674(4)	62(4)
C(16)	1936(6)	8684(5)	3483(4)	52(3)
C(17)	1701(7)	9206(6)	3614(5)	77(5)
C(18)	1283(9)	9498(7)	3445(5)	89(6)
C(19)	1072(7)	9307(6)	3113(4)	76(5)
C(20)	1313(6)	8821(5)	2982(4)	67(4)
C(21)	1749(5)	8497(5)	3143(4)	54(3)
C(31)	1290(6)	7378(7)	2659(3)	60(4)
C(32)	2863(5)	7778(5)	2414(3)	51(3)
C(33)	2197(7)	7070(6)	2178(3)	64(4)
C(1A)	3627(1)	6736(2)	3643(1)	48(3)

C(2A)	3979(1)	7111(2)	3440(1)	48(3)
C(3A)	4510(1)	7328(2)	3576(1)	47(3)
C(4A)	4689(1)	7170(2)	3915(1)	72(4)
C(5A)	4337(1)	6794(2)	4117(1)	68(4)
C(6A)	3806(1)	6577(2)	3982(1)	55(3)
C(1B)	3471(1)	6142(1)	2279(1)	39(3)
C(2B)	3299(2)	5956(2)	1943(1)	49(3)
C(3B)	3628(2)	6125(2)	1649(1)	79(5)
C(4B)	4128(2)	6480(2)	1690(1)	63(4)
C(5B)	4300(2)	6666(2)	2025(1)	72(4)
C(6B)	3971(1)	6497(2)	2319(1)	54(3)
C(1C)	2475(1)	5442(1)	2563(1)	39(3)
C(2C)	1876(1)	5530(1)	2637(1)	39(2)
C(3C)	1471(1)	5075(1)	2578(1)	49(3)
C(4C)	1664(2)	4532(1)	2445(1)	51(3)
C(5C)	2263(2)	4445(1)	2372(1)	71(4)
C(6C)	2668(2)	4899(1)	2431(1)	49(3)
C(1D)	606(1)	5739(2)	3781(1)	46(3)
C(2D)	558(1)	5594(2)	3425(1)	68(4)
C(3D)	118(1)	5204(2)	3313(1)	80(5)
C(4D)	-273(1)	4959(2)	3557(1)	71(5)
C(5D)	-225(2)	5104(2)	3913(1)	76(4)
C(6D)	215(1)	5494(2)	4025(1)	50(3)
C(1E)	916(1)	6981(2)	3868(1)	54(3)
C(2E)	638(1)	7132(2)	3553(1)	59(4)
C(3E)	444(1)	7711(2)	3498(1)	89(5)
C(4E)	528(2)	8139(2)	3758(1)	106(6)
C(5E)	807(2)	7987(2)	4073(1)	92(5)
C(6E)	1001(2)	7408(2)	4128(1)	68(4)
N(1X)	7486(4)	7542(4)	4879(2)	44(2)
C(1X)	9452(5)	6932(6)	4159(3)	49(3)
C(2X)	9391(5)	6558(5)	4501(3)	45(3)
C(3X)	8757(5)	7710(5)	3702(3)	38(2)
C(4X)	8926(5)	8282(5)	3864(3)	43(3)
C(11X)	7116(5)	8042(5)	4724(3)	41(3)
C(12X)	6974(5)	7878(4)	4353(3)	40(3)
C(13X)	7415(5)	7533(5)	4170(3)	38(3)
C(14X)	7286(5)	7393(5)	3815(3)	40(3)
C(15X)	6791(5)	7593(5)	3638(3)	44(3)

C(16X)	6377(5)	7968(5)	3811(3)	47(3)
C(17X)	5892(5)	8201(6)	3624(3)	56(3)
C(18X)	5497(6)	8563(6)	3788(4)	66(4)
C(19X)	5581(6)	8706(6)	4151(5)	73(4)
C(20X)	6047(5)	8495(5)	4323(3)	53(3)
C(21X)	6463(5)	8114(5)	4179(3)	48(3)
C(31X)	7438(6)	8618(6)	4742(3)	57(3)
C(32X)	7097(5)	7016(6)	4945(4)	56(3)
C(33X)	7745(6)	7736(6)	5226(3)	61(3)
C(1F)	8492(2)	6457(1)	3759(1)	38(3)
C(2F)	8073(2)	6057(1)	3885(1)	49(3)
C(3F)	7944(2)	5546(1)	3694(1)	62(4)
C(4F)	8234(3)	5435(2)	3376(1)	71(4)
C(5F)	8654(3)	5835(2)	3250(1)	66(4)
C(6F)	8783(2)	6346(1)	3441(1)	49(3)
C(1G)	9465(1)	7574(1)	4951(1)	40(3)
C(2G)	10004(1)	7420(2)	5104(1)	57(3)
C(3G)	10420(2)	7857(2)	5182(1)	57(3)
C(4G)	10297(2)	8449(2)	5106(1)	78(5)
C(5G)	9758(2)	8603(2)	4952(1)	63(4)
C(6G)	9342(1)	8166(1)	4875(1)	53(3)
C(1H)	8804(2)	6539(1)	5188(1)	42(3)
C(2H)	8971(2)	6693(2)	5529(1)	51(3)
C(3H)	8809(2)	6334(2)	5812(1)	65(4)
C(4H)	8480(2)	5822(2)	5754(1)	78(5)
C(5H)	8313(2)	5667(2)	5412(1)	116(8)
C(6H)	8475(2)	6026(1)	5129(1)	73(4)
C(1I)	8094(2)	9151(1)	3599(1)	51(3)
C(2I)	7912(2)	9413(1)	3914(1)	73(4)
C(3I)	7322(2)	9578(1)	3959(1)	86(5)
C(4I)	6914(2)	9480(2)	3689(1)	94(6)
C(5I)	7096(2)	9218(2)	3375(1)	91(6)
C(6I)	7686(2)	9054(2)	3330(1)	66(4)
C(1J)	9316(2)	9487(1)	3744(1)	60(4)
C(2J)	9394(2)	9530(1)	4108(1)	116(7)
C(3J)	9727(2)	9992(1)	4249(1)	197(15)
C(4J)	9982(2)	10412(2)	4027(1)	122(7)
C(5J)	9905(2)	10370(2)	3664(1)	104(6)
C(6J)	9572(2)	9907(2)	3522(1)	73(4)

Cl(1)	5000	1407(2)	2500	63(1)
O(1)	5093(5)	1795(6)	2192(2)	100(4)
O(2)	4470(6)	1083(6)	2440(4)	122(5)
Cl(2)	5000	8196(4)	2500	139(3)
O(3)	5384(7)	7833(7)	2331(4)	200
O(4)	4718(7)	8511(7)	2271(4)	200
Cl(3)	6732(4)	5416(5)	4492(3)	122(4)
O(5)	7245(8)	5562(12)	4629(7)	150
O(6)	6511(12)	5810(10)	4273(6)	150
O(7)	6293(10)	5384(12)	4754(6)	150
O(8)	6761(12)	4836(8)	4392(7)	150
Cl(4)	8390(5)	9823(4)	5147(3)	111(3)
O(10)	7838(7)	10000	5000	150
O(11)	8590(8)	10394(6)	5186(4)	150
O(12)	8321(10)	9429(10)	5436(5)	150
C(1S)	5432(14)	10000	5000	114(9)
Cl(2S)	5010(6)	9452(4)	4877(2)	234(5)

Table A 17 Crystallographic Data for Complexes (*S,Sp*)-**171a** and (*S,Rp*)-**172a**

Empirical formula	C ₅₂ H ₅₈ F ₁₂ N O P ₅ Pd	
Formula weight	1202.24	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 10.2700(4) Å	α = 88.261(2)°.
	b = 12.2144(4) Å	β = 88.843(2)°.
	c = 21.6001(8) Å	γ = 75.585(2)°.
Volume	2622.82(17) Å ³	
Z	2	
Density (calculated)	1.522 Mg/m ³	
Absorption coefficient	0.588 mm ⁻¹	
F(000)	1228	
Crystal size	0.14 x 0.08 x 0.02 mm ³	
Theta range for data collection	0.94 to 29.48°.	
Index ranges	-14 ≤ h ≤ 13, -16 ≤ k ≤ 16, -29 ≤ l ≤ 29	
Reflections collected	38133	
Independent reflections	26715 [R(int) = 0.0360]	
Completeness to theta = 29.48°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9883 and 0.9222	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	26715 / 23 / 1309	
Goodness-of-fit on F ²	1.066	
Final R indices [I > 2σ(I)]	R1 = 0.0528, wR2 = 0.1194	
R indices (all data)	R1 = 0.0797, wR2 = 0.1442	
Absolute structure parameter	0.00(2)	
Largest diff. peak and hole	1.091 and -0.552 e.Å ⁻³	

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b wR_2 = \sqrt{\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}}, w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP.$$

Table A 18 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complexes (S,Sp)-**171a** and (S,Rp)-**172a**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Pd(1)	3059(1)	4450(1)	3570(1)	20(1)
Pd(2)	4823(1)	10746(1)	9814(1)	21(1)
N(1)	3299(6)	4941(5)	2619(3)	29(1)
N(2)	4467(6)	10607(5)	10794(3)	27(1)
O(1)	4275(6)	5257(4)	6100(3)	45(1)
O(2)	3763(7)	-303(5)	7265(3)	50(2)
P(1)	5310(2)	3622(2)	3869(1)	22(1)
P(2)	2538(2)	3986(1)	4546(1)	21(1)
P(3)	1598(2)	7489(1)	5219(1)	21(1)
P(4)	2630(2)	11482(2)	9444(1)	26(1)
P(5)	5447(2)	11063(1)	8834(1)	22(1)
P(6)	6390(2)	7555(1)	8188(1)	23(1)
P(7)	7838(2)	347(2)	6419(1)	28(1)
P(8)	231(2)	4614(2)	6963(1)	28(1)
P(9)	3964(3)	9486(2)	3053(1)	43(1)
P(10)	4002(3)	5425(2)	344(1)	52(1)
C(1)	1072(7)	5137(5)	3335(3)	20(1)
C(2)	-43(7)	5591(6)	3719(3)	29(2)
C(3)	-1275(8)	6022(6)	3489(3)	33(2)
C(4)	-1521(6)	6016(5)	2860(3)	23(1)
C(5)	-2863(6)	6407(6)	2616(3)	34(1)
C(6)	-3089(6)	6285(6)	2014(3)	39(2)
C(7)	-2015(7)	5838(5)	1615(3)	40(2)
C(8)	-725(6)	5511(5)	1820(3)	34(1)
C(9)	-432(6)	5544(5)	2452(2)	26(1)
C(10)	880(5)	5157(4)	2706(2)	23(1)
C(11)	2087(6)	4716(5)	2291(2)	30(1)
C(12)	2242(7)	3478(6)	2167(3)	45(2)
C(13)	3209(7)	6177(6)	2584(3)	39(2)
C(14)	4574(8)	4374(7)	2293(4)	44(2)

C(15)	6580(7)	2843(6)	3339(3)	27(2)
C(16)	6405(8)	1877(6)	3068(3)	41(2)
C(17)	7309(9)	1303(7)	2629(4)	54(2)
C(18)	8382(11)	1705(8)	2451(4)	64(3)
C(19)	8552(10)	2663(8)	2722(4)	56(2)
C(20)	7679(8)	3249(7)	3157(4)	41(2)
C(21)	6042(7)	4628(6)	4263(4)	25(2)
C(22)	7056(8)	4238(6)	4695(4)	32(2)
C(23)	7480(8)	5061(7)	5044(4)	35(2)
C(24)	6887(8)	6191(6)	4973(4)	34(2)
C(25)	5916(8)	6562(6)	4537(3)	30(2)
C(26)	5490(8)	5787(6)	4187(4)	30(2)
C(27)	5124(8)	2576(6)	4467(4)	32(2)
C(28)	4102(7)	3201(6)	4944(4)	29(2)
C(29)	1407(7)	3054(5)	4629(4)	26(2)
C(30)	1087(8)	2506(6)	4120(4)	31(2)
C(31)	311(9)	1746(6)	4185(4)	35(2)
C(32)	-251(9)	1580(6)	4758(5)	40(2)
C(33)	9(8)	2152(6)	5273(4)	34(2)
C(34)	836(8)	2871(6)	5211(3)	28(2)
C(35)	1846(7)	5176(5)	5066(3)	22(1)
C(36)	2508(7)	6149(5)	4921(3)	22(1)
C(37)	296(7)	8124(5)	4687(3)	22(1)
C(38)	663(8)	8320(5)	4065(3)	27(1)
C(39)	-308(9)	8813(7)	3635(4)	47(2)
C(40)	-1677(10)	9072(6)	3822(4)	50(2)
C(41)	-2024(8)	8864(7)	4438(4)	37(2)
C(42)	-1035(8)	8383(6)	4853(4)	33(2)
C(43)	2759(7)	8352(5)	5275(3)	23(2)
C(44)	2640(7)	9361(6)	4955(3)	26(2)
C(45)	3557(9)	9996(7)	5024(4)	39(2)
C(46)	4598(9)	9649(7)	5432(4)	39(2)
C(47)	4751(8)	8654(7)	5765(4)	32(2)
C(48)	3839(8)	8000(6)	5697(4)	33(2)
C(49)	899(8)	7302(6)	5971(3)	30(2)
C(50)	6742(7)	9979(6)	10100(4)	27(2)
C(51)	7969(7)	9856(5)	9768(3)	28(2)
C(52)	9175(7)	9287(6)	10037(4)	38(2)
C(53)	9245(7)	8915(6)	10662(4)	35(2)

C(54)	10483(7)	8443(6)	10950(4)	48(2)
C(55)	10518(8)	8151(7)	11549(4)	56(2)
C(56)	9347(7)	8278(5)	11896(3)	47(2)
C(57)	8125(6)	8703(5)	11638(3)	34(1)
C(58)	8030(6)	9056(5)	11004(3)	26(1)
C(59)	6785(6)	9551(4)	10706(3)	24(1)
C(60)	5462(6)	9574(5)	11028(3)	28(1)
C(61)	5044(7)	8500(5)	10892(3)	37(2)
C(62)	4803(7)	11614(5)	11059(3)	44(2)
C(63)	3082(8)	10591(8)	11016(4)	50(2)
C(64)	1221(7)	12239(6)	9918(3)	29(2)
C(65)	1162(9)	13318(6)	10108(3)	45(2)
C(66)	126(12)	13847(7)	10512(4)	69(3)
C(67)	-771(9)	13287(7)	10738(4)	54(2)
C(68)	-737(9)	12192(7)	10576(4)	44(2)
C(69)	267(8)	11676(7)	10151(4)	37(2)
C(70)	1995(7)	10398(6)	9080(4)	28(2)
C(71)	2509(8)	9265(6)	9254(4)	32(2)
C(72)	2084(8)	8418(7)	8964(4)	39(2)
C(73)	1112(10)	8712(7)	8515(4)	47(2)
C(74)	554(9)	9837(9)	8354(5)	53(3)
C(75)	979(8)	10681(6)	8635(4)	35(2)
C(76)	2825(8)	12434(5)	8807(3)	26(2)
C(77)	3963(8)	11771(6)	8386(3)	29(2)
C(78)	6575(7)	11986(5)	8747(3)	21(1)
C(79)	6806(8)	12616(6)	9247(4)	30(2)
C(80)	7677(9)	13328(7)	9154(4)	37(2)
C(81)	8249(8)	13462(6)	8583(4)	31(2)
C(82)	7990(8)	12844(6)	8087(4)	33(2)
C(83)	7165(7)	12099(6)	8165(4)	26(2)
C(84)	6244(8)	9814(6)	8397(3)	29(2)
C(85)	5449(8)	8914(5)	8453(4)	28(2)
C(86)	7679(8)	7009(6)	8751(4)	28(2)
C(87)	7405(9)	7084(6)	9376(4)	40(2)
C(88)	8400(8)	6744(6)	9793(4)	46(2)
C(89)	9683(9)	6370(7)	9616(4)	47(2)
C(90)	9988(9)	6246(7)	9025(6)	59(3)
C(91)	9024(8)	6554(6)	8543(4)	35(2)
C(92)	5230(8)	6675(6)	8120(3)	25(2)

C(93)	5386(8)	5706(6)	8496(4)	30(2)
C(94)	4490(8)	5034(7)	8410(4)	39(2)
C(95)	3462(8)	5350(6)	7987(4)	36(2)
C(96)	3323(8)	6332(7)	7641(4)	40(2)
C(97)	4197(8)	7015(6)	7706(4)	33(2)
C(98)	7078(9)	7745(7)	7441(4)	37(2)
C(99)	4984(11)	3537(7)	6651(5)	64(3)
C(100)	5101(8)	4679(6)	6422(4)	33(2)
C(101)	6252(9)	5066(11)	6663(5)	64(3)
C(102)	3130(10)	1429(7)	6726(5)	56(2)
C(103)	2935(9)	314(7)	6927(4)	38(2)
C(104)	1691(11)	17(11)	6762(5)	68(3)
F(1)	7455(5)	-785(4)	6224(2)	42(1)
F(2)	8671(5)	-354(4)	6991(2)	49(1)
F(3)	9159(5)	27(4)	5996(2)	43(1)
F(4)	8219(5)	1466(4)	6617(2)	51(1)
F(5)	7008(5)	1016(4)	5854(2)	48(1)
F(6)	6518(5)	639(5)	6850(3)	54(1)
F(7)	-552(5)	5271(4)	6372(2)	46(1)
F(8)	-133(5)	3491(4)	6760(2)	47(1)
F(9)	1001(5)	3984(4)	7558(2)	49(1)
F(10)	1569(5)	4322(5)	6561(2)	50(1)
F(11)	570(5)	5768(4)	7166(2)	43(1)
F(12)	-1137(5)	4946(4)	7374(2)	39(1)
F(13)	2483(7)	9780(7)	3237(6)	167(5)
F(14)	4199(11)	10266(8)	3595(3)	167(5)
F(15)	5444(7)	9163(7)	2852(5)	157(4)
F(16)	3854(8)	10584(5)	2628(3)	90(2)
F(17)	3722(13)	8827(7)	2489(4)	145(4)
F(18)	4129(8)	8392(5)	3450(2)	94(2)
F(19)	4672(18)	4357(8)	660(6)	253(8)
F(20)	3330(20)	6718(12)	306(11)	381(14)
F(21)	4466(12)	5976(8)	888(3)	144(4)
F(22)	3151(11)	5372(15)	-157(4)	261(9)
F(23)	5077(10)	5641(13)	-40(3)	203(7)
F(24)	2768(12)	5206(13)	714(4)	217(7)

Table A 19 Crystallographic Data for Dichloro Complex (S)-174

Empirical formula	C ₃₄ H ₃₃ Cl ₂ P ₃ Pd S	
Formula weight	743.87	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 12.1188(5) Å	α = 90°.
	b = 8.2274(4) Å	β = 107.051(2)°.
	c = 17.6135(8) Å	γ = 90°.
Volume	1678.98(13) Å ³	
Z	2	
Density (calculated)	1.471 Mg/m ³	
Absorption coefficient	0.940 mm ⁻¹	
F(000)	756	
Crystal size	0.40 x 0.20 x 0.20 mm ³	
Theta range for data collection	1.21 to 34.17°.	
Index ranges	-17 ≤ h ≤ 18, -9 ≤ k ≤ 12, -27 ≤ l ≤ 27	
Reflections collected	23654	
Independent reflections	10200 [R(int) = 0.0218]	
Completeness to theta = 34.17°	93.8 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	10200 / 1 / 370	
Goodness-of-fit on F ²	1.132	
Final R indices [I > 2σ(I)]	R ₁ = 0.0239, wR ₂ = 0.0609	
R indices (all data)	R ₁ = 0.0279, wR ₂ = 0.0765	
Absolute structure parameter	-0.006(14)	
Largest diff. peak and hole	0.535 and -0.387 e.Å ⁻³	

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$

^b $wR_2 = \sqrt{\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}}, w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$

Table A 20 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex (Sp)-**174**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Cl(1)	3954(1)	6190(1)	6872(1)	27(1)
Cl(2)	1083(1)	6159(1)	6923(1)	30(1)
P(1)	3637(1)	2339(1)	6569(1)	22(1)
P(2)	1268(1)	2207(1)	6813(1)	20(1)
P(3)	6623(1)	2285(1)	8734(1)	29(1)
Pd(1)	2467(1)	4255(1)	6782(1)	18(1)
S(1)	7139(1)	71(1)	8610(1)	51(1)
C(1)	-230(2)	2443(3)	6265(1)	23(1)
C(2)	-595(2)	2129(3)	5450(1)	30(1)
C(3)	-1743(2)	2406(4)	5015(2)	37(1)
C(4)	-2508(2)	3011(4)	5386(2)	43(1)
C(5)	-2147(2)	3363(4)	6194(2)	47(1)
C(6)	-1010(2)	3075(4)	6635(2)	36(1)
C(7)	1356(2)	1740(3)	7836(1)	24(1)
C(8)	643(2)	580(3)	8025(2)	37(1)
C(9)	751(3)	212(4)	8814(2)	44(1)
C(10)	1569(3)	983(4)	9410(2)	43(1)
C(11)	2290(2)	2119(4)	9242(2)	41(1)
C(12)	2180(2)	2525(4)	8449(1)	31(1)
C(13)	1770(2)	368(3)	6430(2)	29(1)
C(14)	3101(2)	339(3)	6744(1)	30(1)
C(15)	3675(2)	2335(3)	5546(1)	26(1)
C(16)	2882(2)	3238(4)	4976(2)	43(1)
C(17)	2926(3)	3263(5)	4194(2)	56(1)
C(18)	3763(3)	2369(5)	3988(2)	52(1)
C(19)	4539(2)	1456(4)	4545(2)	43(1)
C(20)	4503(2)	1440(4)	5327(2)	36(1)
C(21)	5139(2)	2390(4)	7182(1)	31(1)
C(22)	5206(2)	2724(3)	8050(1)	30(1)
C(23)	6434(2)	2637(3)	9704(1)	32(1)

C(24)	5588(2)	3656(4)	9816(2)	44(1)
C(25)	5420(3)	3805(5)	10563(2)	59(1)
C(26)	6112(4)	2975(5)	11192(2)	70(1)
C(27)	6993(4)	1993(5)	11091(2)	79(1)
C(28)	7150(3)	1806(4)	10350(2)	56(1)
C(29)	7618(2)	3804(3)	8590(1)	31(1)
C(30)	7291(3)	5276(4)	8216(2)	42(1)
C(31)	8118(3)	6372(4)	8115(2)	53(1)
C(32)	9258(3)	5983(5)	8399(2)	58(1)
C(33)	9609(3)	4557(4)	8793(2)	54(1)
C(34)	8801(2)	3457(4)	8882(2)	43(1)

Table A 21 Crystallographic Data for Complex (Sp)-175

Empirical formula	C ₃₄ H ₃₃ Cl ₂ O ₄ P ₃ Pd Se
Formula weight	854.77
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 10.7452(4) Å α = 90°. b = 10.7665(4) Å β = 90°. c = 30.5990(11) Å γ = 90°.
Volume	3539.9(2) Å ³
Z	4
Density (calculated)	1.604 Mg/m ³
Absorption coefficient	1.875 mm ⁻¹
F(000)	1712
Crystal size	0.40 x 0.20 x 0.20 mm ³
Theta range for data collection	1.33 to 30.86°.
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -44 ≤ l ≤ 44
Reflections collected	76481
Independent reflections	11106 [R(int) = 0.0279]
Completeness to theta = 30.86°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7055 and 0.5208
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	11106 / 0 / 406
Goodness-of-fit on F ²	1.152
Final R indices [I > 2σ(I)]	R ₁ = 0.0284, wR ₂ = 0.0703
R indices (all data)	R ₁ = 0.0355, wR ₂ = 0.0802
Absolute structure parameter	0.012(6)
Largest diff. peak and hole	0.558 and -0.526 e.Å ⁻³

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b wR_2 = \sqrt{\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}}, w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP.$$

Table A 22 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex (Sp)-**175**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	4561(1)	9431(1)	9103(1)	37(1)
Se(1)	2639(1)	10213(1)	9473(1)	45(1)
Cl(1)	5799(1)	10577(1)	9585(1)	56(1)
Cl(2)	8236(1)	5204(1)	7868(1)	67(1)
O(1)	8885(4)	6105(3)	7614(2)	128(1)
O(2)	8234(5)	5499(5)	8307(1)	150(2)
O(3)	7008(4)	5231(6)	7702(1)	156(2)
O(4)	8815(4)	4051(3)	7787(1)	115(1)
P(1)	1768(1)	11062(1)	8914(1)	41(1)
P(2)	3436(1)	8348(1)	8622(1)	41(1)
P(3)	6231(1)	8522(1)	8783(1)	44(1)
C(1)	1305(3)	9909(3)	8511(1)	48(1)
C(2)	2370(3)	9235(3)	8283(1)	51(1)
C(3)	4493(3)	7629(3)	8222(1)	57(1)
C(4)	5643(3)	7198(3)	8466(1)	62(1)
C(5)	6953(2)	9504(3)	8375(1)	47(1)
C(6)	6472(3)	10676(3)	8279(1)	63(1)
C(7)	7036(5)	11398(4)	7958(1)	83(1)
C(8)	8053(4)	10966(4)	7738(1)	77(1)
C(9)	8520(3)	9803(4)	7823(1)	68(1)
C(10)	7984(3)	9074(3)	8145(1)	58(1)
C(11)	7473(3)	7982(2)	9131(1)	51(1)
C(12)	8355(3)	8821(3)	9277(1)	60(1)
C(13)	9324(3)	8440(4)	9546(1)	68(1)
C(14)	9409(4)	7213(4)	9675(1)	74(1)
C(15)	8555(4)	6380(4)	9534(1)	76(1)
C(16)	7580(4)	6740(3)	9265(1)	66(1)
C(17)	2607(3)	7067(2)	8864(1)	44(1)
C(18)	2946(3)	6673(3)	9279(1)	54(1)
C(19)	2369(4)	5622(3)	9460(1)	70(1)

C(20)	1466(4)	5005(3)	9231(1)	71(1)
C(21)	1130(4)	5388(4)	8824(2)	79(1)
C(22)	1697(3)	6427(3)	8637(1)	63(1)
C(23)	2780(3)	12176(2)	8650(1)	46(1)
C(24)	3775(3)	12680(3)	8877(1)	58(1)
C(25)	4557(4)	13535(3)	8675(2)	73(1)
C(26)	4396(4)	13853(3)	8245(2)	77(1)
C(27)	3407(4)	13340(4)	8018(1)	79(1)
C(28)	2601(4)	12505(3)	8217(1)	65(1)
C(29)	333(2)	11802(2)	9083(1)	45(1)
C(30)	-465(3)	12280(3)	8771(1)	61(1)
C(31)	-1570(3)	12831(4)	8901(1)	72(1)
C(32)	-1891(3)	12866(3)	9338(2)	68(1)
C(33)	-1099(4)	12392(4)	9648(1)	69(1)
C(34)	21(3)	11864(3)	9523(1)	58(1)

Table A 23 Crystallographic Data for Complexes **181**

Empirical formula	C ₄₆ H ₄₄ Cl N O ₄ P ₂ Pd
Formula weight	878.61
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P1
Unit cell dimensions	a = 9.8084(4) Å α = 79.220(2)°. b = 13.7477(4) Å β = 88.686(2)°. c = 15.7166(5) Å γ = 89.995(2)°.
Volume	2081.31(12) Å ³
Z	2
Density (calculated)	1.402 Mg/m ³
Absorption coefficient	0.631 mm ⁻¹
F(000)	904
Crystal size	0.10 x 0.10 x 0.10 mm ³
Theta range for data collection	2.08 to 28.38°.
Index ranges	-13 ≤ h ≤ 13, -18 ≤ k ≤ 18, -20 ≤ l ≤ 20
Reflections collected	51004
Independent reflections	19402 [R(int) = 0.0259]
Completeness to theta = 28.38°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9396 and 0.9396
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	19402 / 13 / 997
Goodness-of-fit on F ²	0.994
Final R indices [I > 2σ(I)]	R ₁ = 0.0350, wR ₂ = 0.0784
R indices (all data)	R ₁ = 0.0453, wR ₂ = 0.0832
Absolute structure parameter	-0.021(13)
Largest diff. peak and hole	0.592 and -0.270 e.Å ⁻³

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b wR_2 = \sqrt{\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}}, w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP.$$

Table A 24 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complexes **181**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	9038(1)	2237(1)	1140(1)	40(1)
Pd(2)	8191(1)	7374(1)	6013(1)	41(1)
Cl(1)	2579(2)	9390(1)	3076(1)	103(1)
Cl(2)	4220(2)	4473(1)	8057(2)	122(1)
N(1)	10520(4)	2724(2)	124(2)	63(1)
N(2)	7264(4)	8000(2)	4817(2)	59(1)
O(1)	2817(9)	8622(5)	2602(6)	224(4)
O(2)	2661(10)	10288(5)	2595(7)	268(5)
O(3)	1408(10)	9257(6)	3341(10)	373(9)
O(4)	3602(14)	9373(11)	3504(7)	364(9)
O(5)	3990(9)	3614(5)	7738(6)	234(5)
O(6)	5591(7)	4535(6)	8067(5)	199(3)
O(7)	3996(11)	5273(6)	7432(8)	318(7)
O(8)	3447(13)	4462(9)	8667(6)	331(7)
P(1)	8402(1)	705(1)	795(1)	38(1)
P(2)	7538(1)	1832(1)	2250(1)	38(1)
P(3)	8822(1)	5791(1)	5753(1)	45(1)
P(4)	9383(1)	6954(1)	7220(1)	42(1)
C(1)	9638(4)	3557(2)	1475(2)	45(1)
C(2)	9514(4)	3886(3)	2268(2)	51(1)
C(3)	10053(4)	4763(3)	2385(2)	53(1)
C(4)	10798(3)	5371(2)	1722(2)	48(1)
C(5)	11416(4)	6272(3)	1836(3)	64(1)
C(6)	12159(5)	6827(3)	1202(4)	80(1)
C(7)	12331(5)	6521(3)	402(4)	83(1)
C(8)	11754(5)	5670(3)	258(3)	67(1)
C(9)	10950(4)	5063(2)	907(2)	49(1)
C(10)	10336(4)	4161(2)	804(2)	50(1)
C(11)	10357(5)	3842(3)	-63(2)	67(1)
C(12)	9073(7)	4150(3)	-533(3)	97(2)

C(13)	11908(5)	2469(3)	485(4)	87(2)
C(14)	10441(7)	2344(3)	-690(3)	98(2)
C(15)	6818(3)	599(2)	2234(2)	41(1)
C(16)	7877(3)	-44(2)	1867(2)	36(1)
C(17)	6940(4)	729(3)	107(2)	51(1)
C(18)	6330(5)	1631(4)	-190(3)	75(1)
C(19)	5180(6)	1649(6)	-751(4)	103(2)
C(20)	4743(6)	811(7)	-982(4)	109(2)
C(21)	5340(5)	-67(6)	-685(3)	95(2)
C(22)	6441(4)	-126(4)	-136(2)	64(1)
C(23)	9704(3)	17(2)	325(2)	41(1)
C(24)	9628(4)	-171(3)	-518(3)	57(1)
C(25)	10726(5)	-588(3)	-878(3)	79(1)
C(26)	11882(5)	-816(3)	-423(4)	78(1)
C(27)	11997(5)	-606(3)	406(4)	77(1)
C(28)	10892(4)	-202(3)	778(3)	56(1)
C(29)	7414(3)	-1105(2)	1900(2)	38(1)
C(30)	8369(4)	-1855(3)	1971(2)	51(1)
C(31)	7958(5)	-2834(3)	2046(3)	62(1)
C(32)	6622(5)	-3080(3)	2058(2)	63(1)
C(33)	5659(4)	-2344(3)	1983(3)	62(1)
C(34)	6043(4)	-1366(3)	1898(2)	52(1)
C(35)	6040(4)	2611(3)	2250(2)	47(1)
C(36)	6057(5)	3568(3)	1785(3)	67(1)
C(37)	4880(6)	4152(4)	1776(4)	90(2)
C(38)	3745(6)	3777(4)	2228(4)	95(2)
C(39)	3715(5)	2826(4)	2686(4)	86(2)
C(40)	4846(4)	2252(3)	2697(3)	65(1)
C(41)	8296(3)	1691(2)	3315(2)	43(1)
C(42)	7590(4)	1897(3)	4031(2)	57(1)
C(43)	8232(6)	1772(4)	4821(3)	82(1)
C(44)	9513(7)	1432(4)	4909(3)	90(2)
C(45)	10219(5)	1205(4)	4206(3)	84(1)
C(46)	9609(4)	1351(3)	3396(3)	61(1)
C(47)	7369(4)	8643(2)	6338(2)	47(1)
C(48)	7629(4)	9111(3)	7054(2)	51(1)
C(49)	7003(4)	9950(3)	7156(3)	59(1)
C(50)	6030(4)	10413(3)	6565(3)	59(1)
C(51)	5376(5)	11318(3)	6643(3)	72(1)

C(52)	4472(6)	11741(3)	6059(4)	89(2)
C(53)	4150(5)	11302(4)	5356(4)	87(2)
C(54)	4746(4)	10420(3)	5252(3)	70(1)
C(55)	5729(4)	9967(3)	5838(2)	55(1)
C(56)	6410(4)	9072(2)	5756(2)	51(1)
C(57)	6024(4)	8511(3)	5063(3)	62(1)
C(58)	4858(5)	7802(4)	5396(4)	87(2)
C(59)	8267(5)	8753(3)	4355(3)	76(1)
C(60)	6937(6)	7329(3)	4209(3)	87(2)
C(61)	10076(4)	5703(3)	7266(2)	58(1)
C(62)	9130(4)	5078(2)	6871(2)	54(1)
C(63)	7512(4)	5103(2)	5314(2)	47(1)
C(64)	6290(4)	4893(3)	5777(3)	60(1)
C(65)	5262(5)	4403(4)	5447(4)	81(1)
C(66)	5436(6)	4139(3)	4650(4)	83(1)
C(67)	6594(5)	4370(3)	4176(3)	75(1)
C(68)	7633(5)	4851(3)	4500(3)	61(1)
C(69)	10338(4)	5693(3)	5096(2)	55(1)
C(70)	10785(4)	4787(4)	4910(3)	67(1)
C(71)	11901(5)	4759(5)	4380(3)	89(2)
C(72)	12611(6)	5586(6)	4036(4)	101(2)
C(73)	12219(5)	6489(5)	4225(3)	94(2)
C(74)	11063(4)	6539(4)	4765(3)	72(1)
C(75)	9558(4)	4001(2)	6943(2)	51(1)
C(76)	8546(6)	3287(3)	7061(3)	82(1)
C(77)	8880(8)	2309(4)	7140(4)	111(2)
C(78)	10177(9)	2007(4)	7142(3)	101(2)
C(79)	11183(7)	2700(4)	7037(3)	96(2)
C(80)	10865(5)	3696(3)	6929(3)	73(1)
C(81)	10906(4)	7694(3)	7243(3)	56(1)
C(82)	11013(5)	8647(3)	6769(3)	70(1)
C(83)	12165(7)	9214(5)	6810(4)	99(2)
C(84)	13226(7)	8842(6)	7298(5)	116(3)
C(85)	13190(6)	7909(6)	7751(4)	99(2)
C(86)	12014(4)	7322(4)	7735(3)	72(1)
C(87)	8461(4)	6910(2)	8246(2)	46(1)
C(88)	9074(5)	7134(3)	8971(2)	64(1)
C(89)	8335(6)	7057(4)	9741(3)	87(2)
C(90)	7016(6)	6738(5)	9787(3)	95(2)

C(91)	6399(6)	6473(4)	9076(3)	92(2)
C(92)	7114(4)	6583(3)	8307(3)	67(1)

Table A 25 Crystallographic Data for Dichloro Complex (*R,R*)-**184**

Empirical formula	C ₃₁ H ₃₀ Cl ₄ O ₄ P ₂ Pd	
Formula weight	776.69	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 8.9387(3) Å	α = 97.391(2)°.
	b = 9.6553(3) Å	β = 90.945(2)°.
	c = 10.4811(4) Å	γ = 109.501(2)°.
Volume	843.89(5) Å ³	
Z	1	
Density (calculated)	1.528 Mg/m ³	
Absorption coefficient	0.995 mm ⁻¹	
F(000)	392	
Crystal size	0.10 x 0.08 x 0.05 mm ³	
Theta range for data collection	1.96 to 34.86°.	
Index ranges	-13 ≤ h ≤ 13, -15 ≤ k ≤ 14, -15 ≤ l ≤ 15	
Reflections collected	11892	
Independent reflections	10051 [R(int) = 0.0230]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9519 and 0.9070	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	10051 / 3 / 381	
Goodness-of-fit on F ²	1.005	
Final R indices [I > 2σ(I)]	R ₁ = 0.0478, wR ₂ = 0.0955	
R indices (all data)	R ₁ = 0.0860, wR ₂ = 0.1243	
Absolute structure parameter	-0.05(3)	
Largest diff. peak and hole	0.645 and -0.462 e.Å ⁻³	

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b wR_2 = \sqrt{\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}}, w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP.$$

Table A 26 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex (*R,R*)-**184**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	7450(1)	7539(1)	5112(1)	35(1)
Cl(1)	9661(2)	9729(2)	5198(2)	57(1)
Cl(2)	7359(3)	7715(2)	7361(2)	64(1)
Cl(3)	2294(8)	1127(9)	8952(6)	285(4)
Cl(4)	-271(8)	2379(5)	9138(5)	225(3)
O(1)	6545(5)	4434(5)	361(3)	54(1)
O(2)	4391(5)	5125(5)	498(4)	57(1)
O(3)	3416(5)	2544(4)	2368(4)	60(1)
O(4)	1833(4)	3741(4)	3269(4)	51(1)
P(1)	7447(2)	7131(2)	2960(2)	33(1)
P(2)	5210(2)	5594(2)	4955(2)	34(1)
C(1)	5951(6)	5260(5)	2418(5)	34(1)
C(2)	4499(6)	5136(5)	3215(5)	34(1)
C(3)	3222(6)	3644(6)	2882(5)	40(1)
C(4)	5511(6)	4935(6)	996(5)	39(1)
C(5)	442(8)	2401(8)	2971(9)	77(2)
C(6)	6349(9)	4163(10)	-1019(6)	79(2)
C(7)	6822(6)	8449(5)	2199(5)	35(1)
C(8)	6315(6)	9463(6)	2966(5)	43(1)
C(9)	5853(7)	10506(7)	2415(6)	53(2)
C(10)	5911(8)	10535(6)	1117(6)	56(2)
C(11)	6406(8)	9527(7)	342(6)	58(2)
C(12)	6863(7)	8494(6)	874(5)	46(1)
C(13)	9307(6)	7157(6)	2269(5)	40(1)
C(14)	10334(7)	8465(7)	2009(8)	71(2)
C(15)	11781(9)	8578(8)	1505(9)	83(3)
C(16)	12157(7)	7314(8)	1223(7)	57(2)
C(17)	11156(7)	6001(7)	1487(6)	51(1)
C(18)	9716(7)	5891(7)	2010(6)	47(1)
C(19)	5448(6)	3925(6)	5394(5)	38(1)

C(20)	7008(7)	3912(7)	5578(5)	50(1)
C(21)	7211(10)	2608(9)	5897(6)	70(2)
C(22)	5947(12)	1400(8)	6035(6)	74(2)
C(23)	4427(11)	1408(7)	5851(6)	72(2)
C(24)	4172(8)	2674(7)	5527(6)	53(1)
C(25)	3613(6)	5938(6)	5820(5)	38(1)
C(26)	3272(8)	5471(8)	7014(6)	64(2)
C(27)	2109(11)	5822(11)	7719(9)	87(3)
C(28)	1278(10)	6616(10)	7230(10)	91(3)
C(29)	1638(9)	7109(9)	6067(9)	82(2)
C(30)	2807(8)	6773(7)	5348(7)	59(2)
C(31)	530(20)	990(30)	8636(18)	256(13)