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Asymmetric Synthesis of Chiral Arsine Ligands Promoted by Organopalladium Complexes

Maricar Lim Bungabong

(BSc. Hons, Mapua Inst. of Tech.)

School of Physical and Mathematical Sciences

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TABLE OF CONTENTS

Acknowledgements	ii
Summary	ix
List of Compounds Synthesized	xi
Nomenclature, X-ray Structural Data, Abbreviations and Symbols	xiv
List of Tables	xviii
List of Schemes	xix
List of Figures	xxiii

CHAPTER 1	1
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General Introduction

1.1	Chirality of Life	2
1.2	Biological Properties of Chiral Molecules	3
1.3	Development in Asymmetric Synthesis	5
1.4	Transition Metal Complexes in Asymmetric Synthesis	8
1.5	Bidentate Arsine Ligands	11
1.5.1	Application of Bisarsine Ligands	11
1.5.1.1	Application of Achiral Bisarsine Ligands	12
a.)	Selective Hydrogenation of Dienes to Monoenes	12
1.5.1.2	Application of Chiral Bisarsine Ligands	13
a.)	Asymmetric Hydrogenation of α,β -unsaturated acids	13
b.)	Asymmetric Hydrosilylation	16
1.5.2	Application of Heterobidentate (E-E') Ligands	18

1.5.2.1	Application of As-P Mixed Bidentate Ligand	18
1.5.2.2	Application of As-N Mixed Bidentate Ligand	19
1.6	Preparation of Bisarsine and Hetero-bidentate Arsine Ligands	20
1.6.1	Chiral Building Blocks	21
1.6.1.a	Synthesis of Optically Pure Bisarsine Ligand, Diarsop 21	21
1.6.1.b	Synthesis of the Chiral Hetero-bidentate As-N Ligand, (R_C)-50	22
1.6.2	Optical Resolution	23
1.6.2.a	Preparation of the Bisarsine Ligands, (R^*_{As}, R^*_{As})-52 and (R_{As}, S_{As})-53	23
1.6.2.b	Preparation of the Chiral Hetero-bidentate As-N ligand, (R_{As}/S_{As})-63	25
1.6.2.c	Preparation of the Chiral Hetero-bidentate As-P ligand, (R^*, R^*)-66 and (R^*, S^*)-67	27
1.6.2.d	Preparation of the Chiral Hetero-bidentate As-S Ligand, (R_{As}/S_{As})-76	30
1.6.3	Aymmetric Synthesis	32
1.6.3.a	Preparation of the Chiral As-P Bidentate Ligand, (-)-80	33
1.7	Overview of the Present Study	35

CHAPTER 2 36

[4+2] Diels-Alder Cycloaddition Reaction

2.1	Introduction	37
2.2	Results and Discussion	45

2.2.1	Bis(acetonitrile)-(S)-[9-(1-(dimethylamino)ethyl)-10-phenanthryl]-C,N]palladium(II) perchlorate Promoted Cycloaddition Reaction	45
2.2.2	Regioisomerism of the Products	48
2.2.3	Single Crystal Diffraction Analysis of (<i>R_P</i>)-79	48
2.2.4	Generation of Free Ligand, (<i>S_P</i>)-80	49
2.2.5	(<i>R</i>)-[1-(1-(dimethylamino)ethyl)-2-naphthalenyl-C,N]palladium(II) Promoted Cycloaddition between divinylphenylarsine and DMPP	50
2.2.6	Single Crystal Diffraction Analysis of the Dichloro Complex (<i>S_P</i> , <i>S_{As}</i>)-124	53
2.2.7	Liberation of the Free Ligand (<i>R_P</i> , <i>R_{As}</i>)-125	55
2.3	Conclusion	56
2.4	Experimental Section	57
2.4.1	Instrumentation	57
2.4.2	Reagents	57
2.4.3	Syntheses	58
CHAPTER 3		64

Alkynylarsine Insertion Reaction Into Aryl C-Pd Bond

3.1	Introduction	65
3.2	Results and Discussion	72
3.2.1	Preparation of Diphenyl-1-propynylarsine, 148	72
3.2.2	Insertion of Alkynylarsine in Pd-C Bond	72
3.2.3	X-ray Crsytal Diffraction Analysis of (<i>R_C</i>)-150	73

3.2.4	^1H NMR Spectroscopic Analysis of the Organoplatinum(II) Complex, (R_C)-150	75
3.2.5	Assignments of ^1H NMR Resonance Signals of (R_C)-150: Two- dimensional ^1H - ^1H ROESY NMR Spectroscopy Analysis	77
3.3	Conclusion	81
3.4	Experimental Section	82
3.4.1	Instrumentation	82
3.4.2	Reagents	82
3.4.3	Syntheses	82
CHAPTER 4		86
	<i>Asymmetric Hydroarsination Reaction</i>	
<hr/>		
4.1	Introduction	87
4.2	Results and Discussion	90
4.2.1	Hydroarsination of Diphenylvinylphosphine	90
4.2.1.1	Single Crystal X-ray Crystallography of (S_C)-154a	92
4.2.1.2	Two-dimensional ^1H - ^1H ROESY NMR Spectroscopy Analysis of (S_C)-154a	94
4.2.2	Asymmetric Hydroarsination of Divinylphenylphosphine	100
4.2.2.1	Single Crystal X-ray Diffraction Analysis of (S_C, S_P)-154b and (R_C, R_P)-154	102
4.2.2.2	NMR Spectroscopy Analysis of (S_C, R_P)-154b and (S_C, S_P)-154b	107
4.2.3	Hydroarsination of Diphenyl-1-propynylphosphine and Asymmetric Hydroarsination of Di-1-propynylphenylphosphine	108

4.2.3.1	X-ray Crystallography Analysis of 162	111
4.2.4	Asymmetric Hydroarsination of Diphenyl-1-propenyl-(<i>E</i>)-phosphine	113
4.2.4.1	Single Crystal X-ray Diffraction Analysis of (<i>S_C</i> , <i>R_C</i>)-165	115
4.2.4.2	Mechanistic Study of Asymmetric Hydroarsination Reaction	121
4.2.4.3	Stereochemical Study of the Bidentate Complexes (<i>S_C</i> , <i>R_C</i>)-165 and (<i>S_C</i> , <i>S_C</i>)-165	122
4.2.4.4	Liberation of (+)-1-diphenylphosphino-2-diphenylarsinopropane, (<i>R_C</i>)-169	123
4.2.5	Asymmetric Hydroarsination of Di-1-propenyl-(<i>E</i>)-phenylphosphine	124
4.2.5.1	Single Crystal X-ray Diffraction Analysis	129
4.2.5.1.a	(<i>S_C</i> , <i>R_C</i> , <i>S_P</i>)-172	129
4.2.5.1.b	(<i>S_C</i> , <i>S_C</i> , <i>R_P</i>)-172	133
4.2.5.2	Two-dimensional ¹ H- ¹ H ROESY NMR of (<i>S_C</i> , <i>R_C</i> , <i>R_P</i>)-172	135
4.2.5.3	Stereochemistry of the More Soluble Diastereomers	138
4.2.5.4	Rotation Around the Pd-P Bond	141
4.2.5.5	NMR Spectroscopic Analysis	141
4.2.6	Asymmetric Hydroarsination of Di-1-propenyl-(<i>Z</i>)-phenylphosphine	143
4.2.6.1	Two-dimensional ¹ H- ¹ H ROESY NMR Spectroscopy of (<i>S_C</i> , <i>S_C</i> , <i>S_P</i>)- 176	146
4.2.6.2	Single Crystal X-ray Diffraction Analysis of (<i>S_C</i> , <i>S_C</i> , <i>R_P</i>)-1776	149
4.2.6.3	Stereochemistry of the Formation of the Diastereomers	152
4.3	Conclusion	154
4.4	Experimental Section	155
4.4.1	Instrumentation	155
4.4.2	Reagents	155

4.4.3	Syntheses	156
	References	170
	List of Publication	178
	Appendices	179

Summary

The bis(acetonitrile) (*S*) phenanthrylamine palladium(II) complex (*S_C*)-**116** is used in the [4+2] Diels-Alder cycloaddition reaction between diphenylvinylarsine and DMPP producing two isomeric products in a ratio of 5:1. The bidentate ligand (*S_P*)-**80** is liberated by simple treatment of complex (*R_P*)-**79** with aqueous potassium cyanide. This compound is previously prepared by Aw et. al. using a different organopalladium complex (*S_C*)-**58** and its properties are in good agreement with previous data.¹² On the other hand, the rigid chiral As-P bidentate ligand with chirality on both arsenic and phosphorus atoms is synthesized. (*R*) Naphthylamine palladium(II) complex (*R_C*)-**58** is used to promote the [4+2] Diels-Alder cycloaddition between divinylphenylarsine and DMPP at room temperature. Two diastereomers at almost equal ratio are produced which comprise of As-P bidentate ligands enantiomeric at their stereogenic arsenic atom. The diastereomeric complexes are separated by fractional crystallization and the less soluble diastereomer (*S_P*,*S_{As}*)-**124** is treated with potassium cyanide to liberate the optically pure bidentate ligand (*R_P*,*R_{As}*)-**125**.

In the second chapter of this work we discuss the insertion reaction of the arsinoalkyne **148** within the Pd-C bond of the achiral palladium(II) complex **131** using the platinum complex (*R_C*)-**138**. This demonstrates the reactivity of the relatively strong Pd-C bond of ortho-metalated complex towards insertion of unsaturated bond. The hetero-nuclear complex (*R_C*)-**150** consisting of a 7-membered palladacycle ring is formed adopting a pseudo-boat conformation. The molecular structure and absolute conformation of this complex is confirmed by single crystal X-ray diffraction study. One unique feature of this structure is the long range bond between Pd(1) and As(1) [3.07(0)Å] atoms forming a 5-coordinate palladium center.

Lastly, the novel asymmetric hydroarsination reaction in the synthesis of optically active P-As hetero-bidentate ligands is discussed in this work. Metal complex promoted hydroarsination reaction between diphenylarsine and various alkenyl and alkynyl phosphines is demonstrated. Various types of both achiral and chiral As-P bidentate ligands are prepared. It is observed that the reaction is highly dependent on the polarity of the solvent used. The addition of diphenylarsine is regiospecific wherein the phosphorus atom occupies the coordination site *trans* to nitrogen exclusively. In the asymmetric hydroarsination of dipropenylphosphines leading to bidentate complexes comprising of two chirality centers (stereogenic carbon and phosphorus atom), it is found that only 4 diastereomers are formed as detected by the ^{31}P NMR spectroscopy. These originated from the relative configurations of the newly created stereogenic centers (C and P). The cyclo-palladated rings formed adopt a single conformation. Poor selectivity of the two major diastereomers is observed which is possibly due to the free rotation of monodentate phosphines around the Pd-P bond of its organometallic complex. Generally, the bidentate ligands can be easily liberated from their complexes by treatment with aqueous KCN solution and can be re-coordinated back with the palladium(II) complex without loss of optical purity.

List of Compounds Synthesized

(*S_C*, *R_P*)-117a

(*S_C*, *R_P*)-117b

(*S_P*, *S_{As}*)-124

(*S_P*, *R_{As}*)-124

(*R_C*)-149

(*R_C*)-150

(*S_C*)-154a

(*S_C*, *S_P/R_P*)-154b

162

(*S_C*, *R_C*)-165

(*R_C*)-169

(*S_C*, *S_C*)-165

(*S_C*)-170

(*S_C*, *R_C*, *S_P*)-172

(*S_C*, *R_C*, *R_P*)-172

(*S_C*, *S_C*, *R_P*)-172

(*S_C*, *S_C*, *S_P*)-172

(S_C) -174

(S_C, S_C, S_P) -176

(S_C, S_C, R_P) -176

(S_C, R_C, R_P) -176

(S_C, R_C, S_P) -176

Nomenclature

The names of chemical compounds used in this thesis conform with the format adopted by Chemical Abstracts (Chemical Abstracts, 13th Collective Index, Index Guide, 1992-1996).

X-ray Structural Data

The single crystal X-ray analyses were kindly performed by Dr. Li Yongxin at the Nanyang Technological University (Division of Chemistry and Biological Chemistry).

Abbreviations and Symbols

Anal.	analytical
As	arsenic
ax	axial
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
br	broad
bp	boiling point
<i>c</i>	concentration for O.R.D. analysis
<i>ca</i>	about (Latin <i>circa</i>)
calcd	calculated
C	Celsius

CAMP	cyclohexylo-methoxyphenylmethylphosphine
CDCl ₃	chloroform-d ₁
CD ₂ Cl ₂	dichloromethane-d ₂
COD	1,5-cyclooctadiene
conc	concentrated
d	day(s) (for reaction time)
d	doublet (in NMR assignments)
dd	doublet of doublet (in NMR assignments)
ddd	doublet of doublet of doublet (in NMR assignments)
dec	decomposition
DIARSOP	2,3- <i>o</i> -isopropylidene-2,3-dihydroxy-1,4-bis(diphenylarsino)butane
DIOP	2,3- <i>o</i> -isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane
DiPAMP	1,2-bis[(<i>o</i> -methoxyphenyl)phenylphosphino]ethane
dm	decimeter
DMPP	3,4-dimethylphenylphosphole
DOPA	dihydroxyphenylalanine
<i>E</i>	trans (German <i>entgegen</i>)
ee	enantiomeric excess
e.g.	for example
Et	ethyl
<i>et al.</i>	and others (Latin <i>et alii</i>)

<i>e. g.</i>	example (Latin <i>exempli gratia</i>)
eq	equatorial
<i>etc.</i>	and the rest (Latin <i>et cetera</i>)
g	gram(s)
h	hour(s)
HCl	hydrochloric acid
Hz	Hertz
<i>i.e.</i>	that is (Latin <i>id est</i>)
L	levorotatory
m	multiplet (in NMR assignments)
M	metal type
Me	methyl
mg	milligram(s)
MHz	megaHertz
min	minute(s)
mL	milliliter(s)
mp	melting point
NMR	Nuclear Magnetic Resonance
NOE	Nuclear Overhauser Effect
<i>o</i>	<i>ortho</i>
O.R.D.	Optical Rotation Dispersion
P	phosphorus
Ph	Phenyl
ppm	parts per million
q	quartet (in NMR assignments)

qn	quintet (in NMR assignments)
<i>R</i>	<i>rectus</i> (Latin: absolute configuration)
<i>S</i>	<i>sinister</i> (Latin: absolute configuration)
s	singlet (in NMR assignments)
t	triplet (in NMR assignments)
<i>t</i>	tertiary
THF	tetrahydrofuran
<i>Z</i>	cis (German <i>zusammen</i>)
°	degree of angles
Å	angstrom(s)
ⁿ J _{A-B}	n-bond coupling constant between nuclei A and B
Δ	reflux
σ	sigma bonding
η	helicity in π-bonding ligands
μ	descriptor for bridging
δ	NMR chemical shift in ppm
[α] _D	specific rotation measured at sodium D line (589 nm)

List of Tables

Table 1.1.	Top 10 best selling drugs in 2005
Table 1.2.	Enantiomeric excess of asymmetric hydrogenation products 27(a-c)
Table 1.3.	Enantiomeric excess of asymmetric hydrosilylation products 31(a-c)
Table 1.4.	Enantiomeric excess of asymmetric hydrosilylation products 33(a-c)
Table 2.1.	Selected bond lengths (Å) and angles (°) for complex (S_P, S_{As})- 124
Table 3.1.	Selected bond lengths (Å) and angles (°) for complex (R_C)- 150
Table 4.1.	Selected bond lengths (Å) and angles (°) for complex (S_C)- 154a
Table 4.2.	Selected ^1H NMR δ and integration of the carbon backbone protons of palladium(II) complexes of prophos 151 and diphos
Table 4.3.	Selected bond lengths (Å) and angles (°) for complex (S_C, S_P)- 154b and (R_C, R_P)- 154
Table 4.4.	Selected bond lengths (Å) and angles (°) for complex 162
Table 4.5.	Selected bond lengths (Å) and angles (°) for complex (S_C, R_C)- 165 and (S_C, S_C)- 165
Table 4.6.	^{31}P and ^1H NMR Spectroscopy chemical shifts of selected protons of the diastereomers
Table 4.7.	Selected bond lengths (Å) and angles (°) for complex (S_C, R_C, S_P)- 172 and (S_C, S_C, R_P)- 172
Table 4.8.	^{31}P and ^1H NMR spectroscopy chemical shifts of selected protons of the diastereomers
Table 4.9.	Selected bond lengths (Å) and angles (°) for complex (S_C, S_C, R_P)- 176

List of Schemes

- Scheme 1.1. Asymmetric hydrogenation of a prochiral amino acid for the synthesis of L-DOPA **(4)**.
- Scheme 1.2. Preparation of (-)-menthol via asymmetric allylic isomerization
- Scheme 1.3. Synthetic route for the preparation of (*R*)-alanine via asymmetric hydrogenation reaction
- Scheme 1.4. Selective hydrogenation of 2,3-dimethyl-1,3-butadiene **18**
- Scheme 1.5. Asymmetric hydrogenation of α -acetamidocinnamic acid **22**
- Scheme 1.6. Asymmetric hydrogenation of prochiral amino acids **26(a-c)**
- Scheme 1.7. Reduction of acetophenone to alcohol via asymmetric hydrosilylation
- Scheme 1.8. Asymmetric hydrosilylation of acetophenone **32(a-c)**
- Scheme 1.9. Selective hydrogenation of butadiene **35**
- Scheme 1.10. Asymmetric reduction of *t*-butylmethylketone **40**
- Scheme 1.11. Synthetic route for the preparation of (*R,R*)-(+)-DIARSOP **21**
- Scheme 1.12. Preparation of (*R_C*)-**50** from an optically active amino-alcohol **49**
- Scheme 1.13a. Synthesis of the racemic (**52**) and meso (**53**) chiral diarsine ligand
- Scheme 1.13b. Resolution of (*R*^{*},*R*^{*})-**52** using the palladium(II) complex (*S_C*)-**54**
- Scheme 1.14a. Synthetic route for the preparation of ($\pm$)-**64**
- Scheme 1.14b. Liberation of the optically pure (*R_{As}*/*S_{As}*)-**63**
- Scheme 1.15. Synthetic route for the preparation of diastereomers (*R*^{*},*R*^{*})-**66** and (*R*^{*},*S*^{*})-**67**
- Scheme 1.16a. Liberation of (*S_{As}*,*S_P*)-**66** using the palladium(II) complex (*R_C*)-**54**
- Scheme 1.16b. Liberation of (*S_{As}*,*R_P*)-**67** using the palladium(II) complex (*R_C*)-**58**
- Scheme 1.17a. Synthetic route for the preparation of the chiral As-S ligand ($\pm$)-**74**

- Scheme 1.17b. Resolution of ($\pm$)-**74** using the chiral palladium complex (R_C)-**58**
- Scheme 1.18. Asymmetric Diels-Alder reaction route for the preparation of (-)-**80**
- Scheme 2.1. [4+2] Diels-Alder cycloaddition between DMPP **81** and *N*-phenylmaleimide **82**
- Scheme 2.2. High-pressure Diels-Alder reaction between DMPP **81** and fumaronitrile **85**
- Scheme 2.3 The phosphole oxide as a dienophile in the Diels-Alder cycloaddition reaction between cyclopentadiene **88** and phosphole oxide **87**
- Scheme 2.4 Phosphole oxide acting as a diene on the Diels-Alder cycloaddition between cyclopentadiene **88** and 1,2,5-triphenylphosphole oxide **90**
- Scheme 2.5. Organopalladium(II) promoted cycloaddition between divinylphenylphosphine and DMPP
- Scheme 2.6. [4+2] Diels-Alder cycloaddition between diphenylvinylarsine **107** and DMPP **81** using (*S*) naphthylamine palladium(II) complex **58** as chiral promoter
- Scheme 2.7. [4+2] Diels-Alder Cycloaddition Reaction Involving Cy_2PhAs and DMPP
- Scheme 2.8. [4+2] Diels-Alder Cycloaddition Reaction between diphenylvinylarsine and DMPP using the (*S*) phenanthrylamine palladium(II) complex
- Scheme 2.9. Liberation of the optically pure bidentate ligand (S_P)-**80**
- Scheme 2.10. Chiral organopalladium(II) promoted [4+2] Diels-Alder Cycloaddition Reaction between divinylphenylarsine and DMPP
- Scheme 2.11. Ligand redistribution equilibrium between vinylarsines and DMPP
- Scheme 2.12. Liberation of Chiral Bidentate (R_P, R_{As})-**125**
- Scheme 3.1. Cobalt complex-catalyzed insertion of CO in Co-C bond

- Scheme 3.2. Double insertion of CO into Co-C bond
- Scheme 3.3. Bis-insertion of derivatives of acetylene in Pd-C bonds of various organopalladium(II) complexes
- Scheme 3.4. Insertion reaction between palladium complex-activated phosphinoalkyne (S_C)-**135** and naphthylamine palladium complex (S_C)-**58**
- Scheme 3.5. Insertion reaction between activated phosphinoalkyne (S_C)-**135** and various organoplatinated(II) complex (S_C)-**137/138**
- Scheme 3.6. Synthetic route for the preparation of diphenyl-1-propynylarsine
- Scheme 3.7. Synthetic route for the insertion of diphenyl-1-propynylarsine into Pd-C bond of **131** forming the hetero-metallocyclic (R_C)-**150**
- Scheme 3.8. *Cis-trans* regioisomerism of the platinum complex (R_C)-**138** in solution
- Scheme 3.9. Diastereotopic nature of NMe_2 and CH_2 groups of the dimethylbenzylamine auxiliary in (R_C)-**150**
- Scheme 4.1. Asymmetric Addition Reaction
- Scheme 4.2. Synthetic route for the preparation of (S_C)-**154a** and ($S_C, S_P/R_P$)-**154b**
- Scheme 4.3. Reaction route in obtaining the less soluble epimer (R_C, R_P)-**154**
- Scheme 4.4. Hydroarsination of diphenyl-1-propynylphosphine
- Scheme 4.5. Asymmetric hydroarsination of di-1-propynylphenylphosphine
- Scheme 4.6. Synthetic route for the preparation of ($S_C, R_C/S_C$)-**165**
- Scheme 4.7. Hydrophosphination of the vinylphosphine by the platinum(II) complex of secondary phosphine
- Scheme 4.8. Liberation of (+)-1-diphenylphosphino-2-diphenylarsinopropane, (R_C)-**169**

Scheme 4.9. Synthetic route for the asymmetric hydroarsination of di-1-propenyl-
(*E*)-phenylphosphine with diphenylarsine

Scheme 4.10. Synthetic route for the asymmetric hydroarsination of di-1-propenyl-
(*Z*)-phenylphosphine with diphenylarsine

List of Figures

- Figure 1.1. *R/S* handforms of Linalool
- Figure 1.2. Schematic diagram of the three-point interaction theory of the agonist and the receptor
- Figure 2.1. Chiral phosphine ligands consisting of a rigid phosphabicyclo ring
- Figure 2.2. Molecular structure and absolute configuration of (*R_P*)-**79**
- Figure 2.3. Molecular structure and absolute stereochemistry of (*S_P*,*S_{As}*)-**124**
- Figure 3.1. Molecular structure and absolute configuration of the hetero-nuclear complex (*R_C*)-**150**
- Figure 3.2. 2D-ROESY NMR of (*R_C*)-**150** in CDCl₃. Selected NOE Interactions
- Figure 3.3. (a) Dreiding model of the 5-membered ring conformation of platinum(II) complex, (b) Newmann projection along C(11) and N
- Figure 3.4. Boat conformation of the 7-membered ring
- Figure 4.1. Molecular structure and absolute configuration of (*S_C*)-**154a**
- Figure 4.2. 2D-ROESY NMR spectrum of (*S_C*)-**154a**
- Figure 4.3. Numbering scheme and Dreiding diagram of (*S_C*)-**154a**
- Figure 4.4. ¹H NMR of (*S_C*)-**154a**
- Figure 4.5. Palladium(II) complexes of prophos **155** and diphos **156**
- Figure 4.6. Molecular structure and absolute configuration of (*S_C*,*S_P*)-**154b**
- Figure 4.7. Molecular structure and absolute configuration of (*R_C*,*R_P*)-**154**
- Figure 4.8. The shielding effect of phenyl on phosphorus on H_γ
- Figure 4.9. Molecular structure of **162**
- Figure 4.10. Molecular structure and absolute configuration of the cationic complex (*S_C*,*R_C*)-**165**

- Figure 4.11. Molecular structure and absolute configuration of the cationic complex (S_C, S_C) -**165**
- Figure 4.12. Pathways for the stereoselective formation of the products of asymmetric hydroarsination of 1-propenyl-(*E*)-diphenylphosphine
- Figure 4.13. ^{31}P NMR spectrum of the asymmetric hydroarsination between diphenylarsine and di-1-propenyl-(*E*)-phenylphosphine
- Figure 4.14. Molecular structure and absolute configuration of the cationic (S_C, R_C, S_P) -**172** (Product A)
- Figure 4.15. The comparison of angle N(1)-Pd(1)-As(1) of (S_C, R_C, S_P) -**172** and (S_C, R_C) -**165**
- Figure 4.16. Molecular structure and absolute configuration of the cationic (S_C, S_C, R_P) -**172** (Product D)
- Figure 4.17. 2D-ROESY NMR of (S_C, R_C, R_P) -**172**
- Figure 4.18. Dreiding models of the actual conformations alongside the less stable conformations of the four diastereomeric products
- Figure 4.19. ^{31}P NMR spectrum of the diastereomeric products of di-1-propenyl-(*Z*)-phenylphosphine and diphenylarsine
- Figure 4.20. Dreiding diagram and numbering scheme of (S_C, S_C, S_P) -**176**
- Figure 4.21. 2D ^1H - ^1H ROESY NMR of (S_C, S_C, S_P) -**176**
- Figure 4.22. Molecular structure and absolute configuration of the cationic complex (S_C, S_C, R_P) -**176**
- Figure 4.23. Newman projection of (S_C, S_C, R_P) -**176** on C(28) and As(1)
- Figure 4.24. Reaction pathways for asymmetric hydroarsination of di-1-propenyl-(*Z*)-phenylphosphine with diphenylarsine

CHAPTER 1

General Introduction

1.1 Chirality of life

It is widely known that living organisms consist of chiral molecules, that is, molecules which are mirror images of one another. Interestingly, only one among these pair of chiral molecules exists in a biological system. For example, proteins contain only L- α -amino acids¹³ while most of monosaccharides occurring in mammals contain D-sugars¹³. There are huge numbers of chiral compounds derived from plants which find their way into pharmaceutical drugs, food supplements, flavors, fragrances, etc. An example is linalool (Figure 1.1), a naturally-occurring terpene alcohol found in many flowers and spice plants with many commercial applications, the majority of which are based on its pleasant scent.¹⁴ Both of its enantiomers are found in nature: *S*-linalool is found, for example, as a major constituent of the essential oils of coriander seed, palmarosa and sweet orange flowers while *R*-linalool is present in lavender, laurel, and sweet basil, among others.¹⁴ Each enantiomer evokes different neural responses in humans, and therefore are anthropophilically classified as possessing distinct scents. *S*-linalool is perceived as sweet, floral, petit grain-like and the *R*-form as more woody and lavender-like.¹⁴

Figure 1.1. *R/S* handforms of Linalool

Scientists are constantly investigating the chemical processes in which plants produce biologically active chiral molecules. Although some analogues of these

molecules have been prepared, the synthesis of a single-handed isomer continues to be one of the major challenges in this endeavor.

1.2 Biological Properties of Chiral Molecules

One of the major contributions of molecular chirality was the emergence of chiral drugs. It is widely known that only one of the pair of enantiomers of the chiral drug will deliver the desired result. This can be explained by a three-point interaction of the agonist or substrate with the receptor or enzyme active site. Receptors are chiral molecules too, therefore it is expected that they will bind well to a particular messenger molecule one which should fit perfectly in three point locations. Example is the L-DOPA, an amino acid used to treat Parkinson's disease (Figure 1.2).

Prior to 1982, around 72% of drugs were synthetically prepared and out of these only 40% is chiral.¹⁵ Unlike natural and semi-synthetic drugs (28%), almost 99% were chiral. Most of these naturally derived chiral drugs were sold as single isomer while only 12% of the synthetic chiral drug was marketed in their pure form. This obviously indicates that it was a common practice to market synthetic chiral drugs as racemates.¹⁵ However, the situation now is changing since more and more drugs are marketed in their optically pure form. In 2005, 6 out of the 10 most marketable drugs were chiral, 3 of those chiral drugs were sold in optically pure form (Table 1.1).

Figure 1.2. Schematic diagram of the three-point interaction theory of the agonist and the receptor

Table 1.1. Top 10 best selling drugs in 2005¹⁶

				US\$
	Brand name	Company	Treats:	Billion
1.	Lipitor*	Pfizer	High cholesterol	12.9
		Bristol-Myers Squibb &		
2.	Plavix*	Sanofi Aventis	Heart disease	5.9
3.	Nexium*	Astra-Zeneca	Heartburn	5.7
4.	Seretide/Advair	GSK	Asthma	5.6
5.	Zocor*	Merck	High cholesterol	5.3
6.	Norvasc	Pfizer	High blood pressure	5.0
7.	Zyprexa	Eli Lilly	Schizophrenia	4.7

8.	Risperdal	Johnson & Johnson Abbott Labs & Takeda	Schizophrenia	4.0
9.	Prevacid*	Pharmaceutical	Heartburn	4.0
10.	Effexor	Wyeth	Depression	3.8

* Chiral drugs

The importance of administering an optically pure chiral drug is to prevent any possibility of adverse effects that one of the enantiomers in the racemates may pose (*e.g.* infamous thalidomide incident). The Food and Drug Administration of USA and other countries have imposed strict rules for pharmaceutical companies to make a thorough evaluation of each enantiomer and that only pure and safe forms be sold in the market.

1.3 Development in Asymmetric Synthesis

The importance of obtaining the enantiomerically pure form of a chiral compound cannot be exaggerated not only for its biological activity but also due to present regulations on chiral drugs. Initially, nature was the sole provider of enantiomeric and diastereoisomeric compounds; these form what is known as the “chiral pool”. This pool is comprised of relatively inexpensive, readily available, optically active natural products, such as carbohydrates, hydroxy acids, and amino acids, that can be used as starting materials for asymmetric synthesis.¹⁷ In the past when chiral compounds are needed, chemists have had to use biochemical processes or resort to racemic mixtures followed by laborious resolutions.

The use of enzymes as chiral catalysts in asymmetric synthesis has been recognized for many years. Enzymes are exceptional in three main respects¹⁸: (a) They are extremely versatile and catalyze a broad spectrum of reactions. There is an enzyme-catalyzed equivalent for almost every type of organic reaction. Furthermore, the reactions take place under mild, often room temperature, and neutral pH, conditions that minimize problems of isomerization, racemization, epimerization and rearrangement that often plague traditional methodology; (b) Enzymes are very efficient catalysts. The rates of enzyme-mediated processes can be faster than those of the corresponding non-enzymatic reactions by factors of up to 10^{12} ; (c) Enzymes are generally very selective in terms of the type of reaction catalyzed and with respect to the structure and stereochemistry of the substrate and product. These properties collectively constitute the specificity of an enzyme and are its most important features for asymmetric synthetic exploitation.

However, the use of enzymes as chiral catalysts in organic reactions has also its limitations due to some reasons¹⁸: (a) Some common experimental conditions can have adverse effects on enzymes and microorganisms. These include elevated temperatures, extremes of pH, and the presence of inorganic salts and inhibitors; (b) The organic substrate structures of asymmetric synthetic interest will often be hydrophobic, requiring the addition of organic co-solvents to promote their solubility in the aqueous biochemical reaction media. The presence of excessive levels of organic solvents inactivates enzymes. Despite the high stereospecificity of enzyme catalysts, its development has been surpassed by homogeneous asymmetric catalysts not only because of its sensitivity towards necessary conditions for organic reactions but also due to the unfamiliarity of classical synthetic chemists to basic techniques of

enzymology and biochemistry and the limited availability of enzymes for various chemical reactions.

Prior to 1968, early attempts to mimic nature's biocatalysis through noble metal asymmetric catalysis primarily focused on heterogeneous catalyst that used chiral supports, such as quartz, natural fibers, and polypeptides.¹⁷ Around this year, a new and alternative approach to asymmetric hydrogenation emerged, one which was not based on a heterogeneous catalysis and was the result of two independent occurrences: (a) the discovery by Geoffrey Wilkinson in 1965 of a rapid and practical method to hydrogenate alkenes homogeneously with a rhodium-triphenylphosphine catalyst¹⁹, and (b) the development of methods for making chiral phosphines by Kurt Mislow²⁰. These discoveries coupled with the demand for optically pure amino acids led to the rebirth of asymmetric hydrogenation.

In 1975, the discovery of a highly efficient asymmetric hydrogenation reaction (Scheme 1.1) catalyzed by a rhodium metal comprising a chiral bisphosphine ligand DiPAMP **1** had facilitated the industrial synthesis of the amino acid L-DOPA **4**, which is known to be useful in treating Parkinson's disease.^{21, 22}

(R,R)-DiPAMP

1

Scheme 1.1. Asymmetric hydrogenation of a prochiral amino acid for the synthesis of L-DOPA (**4**).

1.4 Transition Metal Complexes of Bisphosphines in Asymmetric Synthesis

In the initial investigation in the preparation of L-DOPA, the catalytic system used was $Rh(CAMP)_2COD$ ($CAMP$ = cyclohexylo-methoxyphenylmethylphosphine) where $CAMP$ is a monodentate phosphine ligand.²³ An *ee* of 90% was obtained. However, when the ligand was changed to the bidentate DiPAMP **1**, the *ee* improved to 95%.²³ Following the success of this study on phosphine ligands huge number of other chiral bisphosphines with various chirality centers (such as C^* , P^* or both, axial, etc.) were later synthesized and investigated.

The cationic BINAP-Rh complex **5**, developed by the group of Noyori²⁴, was used in the asymmetric isomerization of allylic amines, which accomplished the industrial synthesis of (-)-menthol from myrcene (Scheme 1.2). The key step in this reaction was the asymmetric isomerization of geranyldiethylamine **7** catalyzed by (*S*)-BINAP-Rh complex **5**.²⁴

Scheme 1.2. Preparation of (-)-menthol via asymmetric allylic isomerization

Asymmetric hydrogenation of prochiral olefins reported in 1971 by Kagan²⁵ and co-workers gave the most promising *ee* during that time. Here the group used the chiral bisphosphine ligand, (*R,R*)-DIOP^{25, 26} **12**, which possesses chirality centers

within the backbone of the bidentate ligand, to obtain (*R*)-*N*-phenylacetylalanine **14** (Scheme 1.3).

Scheme 1.3. Synthetic route for the preparation of (*R*)-alanine via asymmetric hydrogenation reaction

Several other bidentate ligands, such as those containing bisarsine or mixed pnictogen donor atoms (*i.e.* As-As, As-P, As-N), have also proven to be effective in various asymmetric reactions. As will be shown below, chiral bidentate ligands

containing arsenic donor atoms give better selectivities. Sometimes when arsine auxiliaries are used to replace their phosphine analogues, opposite isomers or enantiomers are produced in a variety of catalytic reactions.

1.5 Bidentate Arsine Ligands

The large number of research and application of chiral bisphosphine ligands in transition metal complexes have provided a highly stereoselective optical yield in various key asymmetric reactions (asymmetric hydrogenation, asymmetric isomerization, asymmetric hydrosilylation, *etc.*). These chiral bidentate ligands have a rigid conformation and stay firmly bonded to the metal which provided asymmetric catalysis a high degree of stereoselectivity.²⁶ The study, however, on the analogous bidentate arsine ligands is not as extensive as chiral bisphosphines although it has been known that tertiary arsine sometimes have advantages over tertiary phosphines. The uncatalyzed thermal barrier to inversion of tertiary arsines is about 42-43 kcal mol⁻¹, which is around 14 kcal mol⁻¹ more stable than tertiary phosphines, also they are generally less air-sensitive. It is one of the objectives of the present study to further explore the asymmetric synthesis of chiral bidentate arsine ligands and its nature.

1.5.1 Application of Bisarsine Ligands

Bisphosphine ligands have enjoyed prominence in the area of asymmetric catalysis. This is in contrast to the bidentate arsine ligand, which has proven to be superior in certain catalytic reactions. Several examples are highlighted below.

1.5.1.1 Application of Achiral Bisarsine Ligands

a.) Selective Hydrogenation of Dienes to Monoenes

In earlier catalytic studies, the achiral catalyst of the form $[\text{Rh}(\text{NBD})\text{L}_2]^+\text{A}^-$ (NBD=Norbornadiene, $\text{L}_2=\text{dpae}$ **16** or diphos **17**, $\text{A}=\text{PF}_6$) had found to be effective in selective hydrogenation of dienes to monoenes.²⁷

The hydrogenation of 2,3-dimethyl-1,3-butadiene **18** to the corresponding monoenes using dpae ($\text{Ph}_2\text{As}(\text{CH}_2)_2\text{AsPh}_2$) **16** as ligand showed higher selectivity than the corresponding phosphine analogue, diphos ($\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$) **17** (Scheme 1.4). Furthermore, the formation of the opposite isomer was favored by the arsine ligand, dpae.²⁷

Scheme 1.4. Selective hydrogenation of 2,3-dimethyl-1,3-butadiene 18

1.5.1.2 Application of Chiral Bisarsine Ligands

a.) Asymmetric Hydrogenation of α,β -unsaturated acids

The Rhodium(I) complex of the chiral auxiliary (-)-2,3-*o*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylarsino)butane, (*R,R*)-(+)-diarsop²⁸ **21**, the arsenic analog of (*R,R*)-(-)-diop^{25, 26} **12**, in the presence of large excess triethylamine, was found to yield a lower selectivity of 39% in the asymmetric hydrogenation of α -acetamidocinnamic acid **22** but yielded the opposite *S* absolute configuration of the isomer (Scheme 1.5).^{26,}

29

DIARSOP

(*R,R*)-(+)-**21**

(*S,S*)-(-)-21*N*-acetyl-(*S*)-phenylalanine*ee* 39% chemical yield 50% **(*R,R*)-(-)-12***N*-acetyl-(*R*)-phenylalanine*ee* 85% chemical yield 96%**Scheme 1.5. Asymmetric hydrogenation of α -acetamidocinnamic acid **22****

The Rhodium(I) complex containing (*S,S*)-(-)-1,2-phenylene-bis(methylphenylarsine), (*S,S*)-(-)-diphs (*S,S*)-**24** was found to outperform its phosphorus analogue, (*S,S*)-(-)-diph (*S,S*)-**25**, in most cases (Scheme 1.6). As shown in Table 1.2, an *ee* as high as 90% was obtained for the asymmetric hydrogenation of the prochiral enamide **26c**.³⁰

Scheme 1.6. Asymmetric hydrogenation of prochiral amino acids 26(a-c)

Table 1.2. Enantiomeric excess of asymmetric hydrogenation products 27(a-c)

Optically pure product	(<i>S,S</i>)-(-)- 24	(<i>S,S</i>)-(-)- 25
27a	80%(<i>S</i>)	79%(<i>S</i>)
27b	77%(<i>S</i>)	64%(<i>S</i>)
27c	90%(<i>S</i>)	94%(<i>S</i>)

b.) Asymmetric Hydrosilylation

In the reduction of the derivatives of ketone **28(a-c)** to the corresponding alcohol **31(a-c)**, a catalytic system composed of (-)/(+)-diarsop **21** and the rhodium complex $[\text{Rh}(\text{COD})\text{Cl}]_2$ in benzene was utilized (Scheme 1.7).²⁸ The *ee* of the product varies largely with different silanes and only slightly with different derivatives of ketone used (Table 1.3). However, generally, the efficiency of the DIARSOP ligand in inducing optical purity towards asymmetric reduction of acetone is not of preparative advantage.

Scheme 1.7. Reduction of acetophenone to alcohol via asymmetric hydrosilylation

Table 1.3. Enantiomeric excess of asymmetric hydrosilylation products **31(a-c)**

Optically pure product	(<i>S,S</i>)-(-)- 21	(<i>R,R</i>)-(+)- 21
31a	20%(<i>R</i>)	26%(<i>S</i>)
31b	42%(<i>R</i>)	35%(<i>S</i>)

31c	31%(<i>R</i>)	22%(<i>S</i>)
------------	-----------------	-----------------

The chiral bisarsine ligand, (*S,S*)-(-)-**24**, has also been studied in the asymmetric hydrosilylation of various derivatives of ketone **32(a-c)** (Scheme 1.8).³¹ The *ee* of the asymmetric hydrosilylation of acetophenone **32a** when (*S,S*)-**25** was used is better than that with the bisarsine ligand, DIAS-**24** (Table 1.4). However, the opposite is true when 3,3-dimethylbuta-2-one **32b** was used wherein 32% *ee* was obtained. Lowering the reaction temperature generally improves the *ee*. In the case where the functionalized ketone derivative, 1-(2-methoxyphenyl)ethanone **32c** was used almost no asymmetric induction was observed for both ligands.

Scheme 1.8. Asymmetric hydrosilylation of acetophenone (32a-c)

Table 1.4. Enantiomeric excess of asymmetric hydrosilylation products 33(a-c)

Optically pure product	Temperature (°C)	(<i>S,S</i>)- 24	(<i>S,S</i>)- 25
33a	25	18%	32%
	-78 – 25	36%	-

33b	25	32%	4%
	0 – 25	41%	-
33c	25	2%	1%

It is interesting to note that the asymmetric hydrosilylation reaction proceeded at a faster rate even at ambient temperature. The rate at which the reaction was completed was 5 min for the reaction involving acetophenone **32a** and 1-(2-methoxyphenyl)ethanone **32c**.^{31, 32}

1.5.2 Application of Hetero-bidentate (E-E') Ligands

In asymmetric catalysis the different steric and electronic properties of donor atoms in bidentate ligands are significant factors in determining the potential of a particular catalyst. A relatively small number of studies on the application of these ligands has been done compared to the chiral bisphosphine ligands. One reason for this is its inefficiency in achieving high *ee* in most asymmetric reactions.

Some examples of applications of hybrid E-E' (where E=As, E'=P, N, etc.) ligands in asymmetric synthesis are discussed below.

1.5.2.1 Application of As-P Mixed Bidentate Ligand

The hetero-bidentate As-P ligands are relatively rare, however, their use in asymmetric synthesis had proven valuable in some instances²⁷. For example, in the

reduction of butadiene derivatives arphos **34** had shown that it could give better selectivity in comparison with diphos **17** (Scheme 1.9).²⁷

Scheme 1.9. Selective hydrogenation of butadiene 35

1.5.2.2 Application of As-N Mixed Bidentate Ligand

In the reduction of *t*-butylmethylketone **40** by diphenylsilane using (*S*)-amars **39** the optical yield is only 8% (Scheme 1.10). The observed low selectivity is attributed to the two independent cations with different conformations in the unit cell. The X-ray structural analysis of the Rh-amars complex **39** reveals that the metallocycle adopts two independent cations with different conformations in the unit cell.³³ Each consisted of phenyl rings in pseudo axial-equatorial arrangements, in one cation the equatorial rings exposes its face to the *cis* coordination site while the axial ring displays its edge. The opposite is true for the other cation.

(S)-amars

39

Scheme 1.10. Asymmetric reduction of *t*-butylmethylketone **40**

1.6 Preparation of Bisarsine and Hetero-bidentate Arsine Ligands

A variety of chiral bisphosphines with the general formulae **42-45** (where E = E' = P) have been reported.³⁴ These general formulae of chiral bidentate ligands also describe the diarsine and hetero-bidentate arsine ligands that are known today.

42

43

44

45

(* denotes chiral center)

Based on the standard synthesis of enantiomerically pure compounds, arsine ligands can be prepared via three different synthetic methodologies:

1.6.1 Chiral building blocks

The use of a naturally-occurring chiral entity as starting material is a classical and convenient approach in obtaining a target molecule. However, there is no assurance that the resulting chiral molecule will be enantiomerically pure. Thus, proper design of reaction sequences and conditions are necessary to avoid racemization. One major disadvantage of this method is the limited range of easily-accessed compounds.

1.6.1.a Synthesis of Optically Pure Bisarsine Ligand, Diarsop **21**

The chiral bidentate (*R,R*)-Diarsop **21** was synthesized by the reaction of 1,4-ditosyl-2,3-*o*-isopropylidene-D-threitol **46** with potassium diphenylarsenide dioxanate

47 in a mixture of THF and dioxane at low temperature of 5-15 °C (Scheme 1.11). The resulting product was obtained as white air-stable prisms in moderate yield.²⁹

Scheme 1.11. Synthetic route for the preparation of *(R,R)*-(+)-DIARSOP **21**

It should be noted that DIARSOP *(R,R)*-**21** is an analogue of the well-known chiral diphosphine ligand, DIOP *(R,R)*-**12** which was prepared and tested by Dang and Kagan in 1971. This optically pure diphosphine ligand was prepared from the naturally occurring (+)-tartaric acid.³⁵

1.6.1.b Synthesis of the Chiral Hetero-bidentate As-N Ligand, *(R_C)*-**50**

The treatment of the *(S)*-2-amino-3-methyl-1-butanol **49** with the *o*-cyano arsine ligand **48** in the presence of ZnCl₂ resulted in a condensation reaction followed by cyclization to form the optically pure oxazoline functionalized As-N hetero-bidentate ligand *(R_C)*-**50** (Scheme 1.12).³⁶

Scheme 1.12. Preparation of *(R_C)*-**50** from an optically active amino-alcohol **49**

1.6.2 Optical Resolution

Resolution usually gives rapid access to both enantiomers of a biologically important molecule. However, it is generally inefficient and tedious. It has, however, provided an alternative route for some important chiral molecules which could not be obtained by asymmetric synthesis.

1.6.2.a Preparation of the Bisarsine Ligands, (R^*_{As}, R^*_{As})-**52** and (R_{As}, S_{As})-**53**

The diastereomeric ligand *o*-phenylenebis(methylphenylarsine), (R^*_{As}, R^*_{As})-**52** and (R_{As}, S_{As})-**53**, were prepared through the reaction between dichlorobenzene **51** and methylphenylarsenide ion in 1:2 ratio in THF (Scheme 1.13a).³⁷ A mixture of racemic and meso products were obtained. The racemic diastereomers crystallized out from a solution of diethyl ether and methanol while the meso isomer remained in the mother liquor. This solution was treated with NiCl_2 to form $[(R,S)\text{-53}]_2\text{NiCl}]\text{Cl}$ which is less soluble than the analogous complex of the diastereomers in ethanol.³⁷

Scheme 1.13a. Synthesis of the racemic (**52**) and meso (**53**) chiral diarsine ligand

Resolution of the racemic mixture using the chiral organo-palladium dimer (S_C)-**54** allows the separation of the less soluble diastereomeric complex (S_C, S_{As}, S_{As})-**56** through crystallization (Scheme 1.13b). Treatment with HCl and subsequently with aqueous KCN liberated the optically pure diarsine (R_{As}, R_{As})-**52** as air-stable crystals (Scheme 1.13c).³⁷

Resolution

Scheme 1.13b. Resolution of (R^*, R^*)-**52** using the palladium(II) complex (S_C)-

Liberation

Scheme 1.13c. Liberation of (R_{As}, R_{As}) -52** using conc. HCl and aqueous KCN**

1.6.2.b Preparation of the Chiral Hetero-bidentate As-N ligand, (R_{As}/S_{As}) -**63**

As illustrated in Scheme 1.14, 1,3-dimethyl-2-[2-(dimethylarsino)phenyl]-imidazolidine **59** was oxidized by acid catalysis to form 2-(dimethylarsino)benzaldehyde **60**. The aldehyde was reduced to the corresponding alcohol. This was then lithiated twice to protect the hydroxyl group each time it is treated with sodium in liquid ammonia. Finally $(\pm)$ -**62** was treated with 2-chloroethamine to obtain the racemic amino-arsine bidentate ligand $(\pm)$ -**63**. This racemic ligand was resolved using the chiral palladium(II) complex (R_C) -**58** followed by isolation of the resulting diastereomers through re-crystallization (Scheme 1.14a). Each isolated diastereomer was then treated with 1,2-diaminoethane to liberate the optically pure ligand (R_{As}) -**63** and (S_{As}) -**63** (Scheme 1.14b).³⁸

(*R_C*)-58

Scheme 1.14a. Synthetic route for the preparation of (±)-64

Scheme 1.14b. Liberation of the optically pure (R_{As}/S_{As}) -63

1.6.2.c Preparation of the Chiral Hetero-bidentate As-P ligand, (R^*, R^*) -66 and (R^*, S^*) -67

The As-P ligands $(\pm)$ -phas-**66-67** were prepared by treating 1,2-dichlorobenzene **51** with sodium methylphenylphosphide and subsequently by sodium methylphenylarsenide (Scheme 1.15). The resulting bis(tertiary) product was obtained in fairly high yield as viscous oil through distillation. The two diastereomeric products (R^*, R^*) -**66** and (R^*, S^*) -**67** were separated by careful fractional crystallization using hot methanol.

Scheme 1.15. Synthetic route for the preparation of diastereomers $(R^*,R^*)\text{-66}$ and $(R^*,S^*)\text{-67}$

The enantiomers of $(R^*,R^*)\text{-66}$ were resolved using the chiral phenylene palladium(II) complex $(R_C)\text{-54}$. The addition of excess aqueous NH_4PF_6 precipitated $(R_C,R_{As},R_P)\text{-69}$ as colorless prisms. Treating the ionic complex with concentrated HCl and subsequently with aqueous KCN liberated $(S_{As},S_P)\text{-66}$ as colorless air-stable prisms (Scheme 1.16a).³⁹

Scheme 1.16a. Liberation of $(S_{As},S_P)\text{-66}$ using the palladium(II) complex $(R_C)\text{-54}$

54

The resolution of $(R^*,S^*)\text{-67}$ was achieved using the naphthalenic analogue $(R_C)\text{-58}$ as the resolving agent. The diastereomeric mixture obtained was treated with excess NH_4PF_6 to selectively precipitate the cationic complex $(R_C,R_{As},S_P)\text{-71}$ as colorless prisms. To liberate the optically pure bidentate ligand $(S_{As},R_P)\text{-67}$, the ionic complex was treated with concentrated H_2SO_4 to cleave off the amine auxiliary and then with LiCl to finally obtain the dichloro complex. This complex was treated with aqueous KCN (Scheme 1.16b).³⁹

Scheme 1.16b. Liberation of $(S_{As}, R_P)\text{-67}$ using the palladium(II) complex $(R_C)\text{-58}$

58

1.6.2.d Preparation of the Chiral Hetero-bidentate As-S Ligand, $(R_{As}/S_{As})\text{-76}$

The racemic tertiary arsine, $(\pm)\text{-2-(mercaptoethyl)methylphenylarsine } (\pm)\text{-74}$ was prepared by adding ethylene sulfide **72** into sodium methylphenylarsenide in THF.⁴⁰ The ligand was obtained in good yield as air-sensitive colorless oil (Scheme 1.17a).

Scheme 1.17a. Synthetic route for the preparation of the chiral As-S ligand (±)-

74

The resolution was carried out by adding 2 mole equivalence of the resolving agent (*R_C*)-**58** in 1 equivalence of the racemic tertiary arsine (±)-**74** in dichloromethane. The reaction yields epimers (Scheme 1.17b), which were then separated by re-crystallization of the mixture from dichloromethane-acetone system. The least soluble di-nuclear complex (*R_C*,*S_{As}*,*S_S*,*R_C*)-**75** was isolated as yellow prisms. The more soluble epimer (*R_C*,*R_{As}*,*R_S*,*R_C*)-**75** was not isolated in its solid form. The isolated epimer was then treated with 1,2-diaminoethane to obtain the mono-nuclear complex (*R*,*S_{As}*)-**76**. This complex when treated with aqueous KCN liberated the optically pure ligand **74**.⁴⁰

Scheme 1.17b. Resolution of $(\pm)\text{-74}$ using the chiral palladium complex $(R_C)\text{-58}$

1.6.3 Asymmetric Synthesis

The earliest example of asymmetric synthesis is found in enzymatic transformations. High interests on this synthetic technique had brought about a large number of asymmetric reactions and relatively fewer industrial applications. In catalysis, a very small amount of chiral auxiliary can produce the desired material in many fold, such that in some cases recycling of the catalyst may be deemed unnecessary. The synthesis of new and potential chiral auxiliaries such as phosphine,

arsine and mixed phosphorus-arsenic ligands are usually prepared through asymmetric synthesis using chiral catalysts present stoichiometrically. The example below demonstrates the use of stoichiometrical amount of the chiral organo-palladium complex for the asymmetric synthesis of chiral bidentate ligands.

1.6.3.a Preparation of the Chiral As-P Bidentate Ligand, (-)-**80**

The first asymmetric synthesis of a rigid As-P hetero-bidentate species with one phosphorus and three carbon stereogenic centers was carried out by the group of Leung⁴¹. This new chiral dissymmetrical bidentate ligand was prepared using organo-palladium complex (*S_C*)-**58** via Diels-Alder cycloaddition reaction. It was reported that only a single isomeric product, (+)-**78** was detected by ³¹P NMR spectroscopy. This diastereomer was treated with concentrated HCl to convert it to its dichloro complex (-)-**79** and subsequently treated with aqueous KCN to liberate the optically pure (-)-**80** (Scheme 1.18).

Scheme 1.18. Asymmetric Diels-Alder reaction route for the preparation of (-)-

80

There is also report on the asymmetric synthesis of similar rigid As-P bidentate ligand from the Diels-Alder cycloaddition reaction involving dicyclohexylvinylarsine as dienophile.⁴² They studied the differences in selectivity of using three different types of chiral auxiliaries. The details of which will be discussed in the succeeding chapter.

1.7 Overview of the Present Study

The study of chiral bidentate or hetero-bidentate phosphine ligands is well established. The number of chiral phosphine ligands clearly outnumbered chiral bidentate arsine ligands. Due to the relatively few known arsine ligands, its catalytic properties are not also well studied. It is my goal to synthesize new kinds of chiral As-P bidentate ligands and to study their unique properties.

Accordingly, this thesis is divided into three chapters. Chapter 2 deals with the extension of the previous work of our group on the organo-palladium promoted Diels-Alder cycloaddition reaction wherein in this work DMPP and divinylphenylarsine are used to generate chirality centers on both phosphorus and arsenic atoms. Chapter 3 deals with the study of the organo-platinum complex activated insertion of C-C triple bond of an alkynylarsine within the C-Pd bond of an achiral organo-palladium complex. Lastly, Chapter 4 presents the novel asymmetric hydroarsination reaction as a new and alternative technique of preparing chiral dissymmetric As-P bidentate ligands having chirality either on carbon, phosphorus, or both.

CHAPTER 2

[4+2] Diels-Alder Cycloaddition Reaction

2.1 Introduction

The first successful Diels-Alder reaction of a phosphole was between 1-phenyl-3,4-dimethylphosphole (DMPP) **81** and *N*-phenylmaleimide **82** which gave the crystalline cycloadduct **83** in 50% yield (Scheme 2.1).^{43, 44} The susceptibility of maleimides to Diels-Alder reaction facilitated the formation of the cycloaddition product in mild condition. The cycloadduct **83** has its phenyl group on the phosphorus bridge in *anti* position with the alkene moiety and the 5-membered ring fused in the *endo* orientation.

Scheme 2.1. [4+2] Diels-Alder cycloaddition between DMPP **81 and *N*-phenylmaleimide **82****

The [4+2] cycloaddition reaction between DMPP **81** and fumaronitrile **85** under high pressure conditions was satisfactorily conducted.⁴⁵ The reaction proceeded at 67.5×10^6 mmHg and 30 °C for 24 hours to give colorless crystals of **86** in 67% yield (Scheme 2.2).⁴⁵

Scheme 2.2. High-pressure Diels-Alder reaction between DMPP 81 and fumaronitrile 85

In the Diels-Alder reaction between cyclopentadiene **88** and 1-phenylphosphole oxide **87**, the penta-valent phosphole can either act as a diene or dienophile depending on its substituents. The reaction between 1-phenylphosphole oxide **87** and cyclopentadiene **88** at 20 °C yielded a cycloadduct **89** in which the phosphole reacted as a dienophile (Scheme 2.3).⁴⁶

Scheme 2.3 The phosphole oxide as a dienophile in the Diels-Alder cycloaddition reaction between cyclopentadiene 88 and phosphole oxide 87

However, when 1,2,5-triphenylphosphole oxide **90** was reacted with cyclopentadiene **88**, it was found that the phosphole oxide acted as a diene. The product **91** was obtained as white needles in 40% yield (Scheme 2.4).⁴⁶

Scheme 2.4 Phosphole oxide acting as a diene on the Diels-Alder cycloaddition between cyclopentadiene 88 and 1,2,5-triphenylphosphole oxide 90

One very interesting fact about phosphole derivatives is that their coordination in various metal complexes had made possible the Diels-Alder reaction of several dienophiles.⁴³ Wild and Nelson and their co-workers⁴² have pointed out few advantages of using chiral metal complexes in the [4+2] Diels-Alder cycloaddition reactions involving phospholes. Firstly, the asymmetric synthesis of cycloadducts derived from phospholes using chiral metal complexes exhibits diastereoselectivity. The chiral products obtained from these reactions can be easily isolated in their optically pure forms by simple manipulations such as column chromatography or fractional crystallizations. Secondly, several pairs of racemic diastereomers (*syn-endo*, *syn-exo*, *anti-endo* and *anti-exo*) that are initially obtained can be reduced to a single *syn-exo* diastereomer that is produced by intramolecular cycloaddition within the coordination sphere of the chiral palladium template.⁴²

Our group has reported a series of stereoselective synthesis of various types of optically pure rigid diphosphine ligands with chirality either on phosphorus or carbon backbones or both (Figure 2.1).

Figure 2.1. Chiral phosphine ligands consisting of a rigid phosphabicyclo ring

All these ligands were prepared asymmetrically using various derivatives of chiral organopalladium(II) complexes as reaction promoters. These complexes enable the cycloaddition reaction between DMPP **81** and various non-functionalized dienophiles to be carried out under mild conditions. For example, in previous work

from our group, the reaction rate could be as fast as 2 hours for cycloaddition reactions between DMPP and tertiary vinylphosphines as dienophile.¹¹

The importance of the chiral auxiliary in the metal complex has been highlighted by our group.² Only one diastereomer was produced in the cycloaddition reaction between DMPP and divinylphenylphosphine using the (*S*) naphthylamine palladium(II) complex (*S_C*)-**58** as the chiral inductor (Scheme 2.5). This is in contrast to previous work⁴⁷, which used PdCl₂ and yielded two diastereomers epimeric at the vinylic phosphorus. It appears that the H γ of the naphthylamine auxiliary (*S_C*)-**58** provided the steric control on the phosphine moiety hence causing it to produce a single isomeric form of the cycloadduct.

Scheme 2.5. Organopalladium(II) promoted cycloaddition between divinylphenylphosphine and DMPP

In 1996, the first rigid asymmetric As-P bidentate ligand (*S_P*)-**80** was synthesized by Aw *et al.* in our group.¹² The reaction between diphenylvinylarsine **107** and 1-phenyl-3,4-dimethylphosphole **81** proceeded at room temperature in acetonitrile (Scheme 2.6). This was briefly discussed in the last part of the general introduction.

Scheme 2.6. [4+2] Diels-Alder cycloaddition between diphenylvinylarsine **107** and DMPP **81** using (*S*) naphthylamine palladium(II) complex **58** as chiral promoter

Investigation of the crude product mixture by ^{31}P NMR spectroscopy revealed two sharp singlets: δ 118.1 and 119.0 in 5:1 diastereomeric ratio.¹² The large downfield shift of the cycloaddition products is indicative of the formation of the *syn* 7-phosphanorbornene compound.⁴⁸

The groups of Wild and Nelson⁴² reported similar [4+2] Diels-Alder cycloaddition involving dicyclohexylarsine **110** and DMPP using chiral organopalladium(II) complexes of three different orthometallated auxiliaries (Scheme 2.7). The cycloaddition reaction using the (*S*) phenylamine palladium complex (*S_C*)-**109** produced four isomers consisting of 2 regioisomers and 2 diastereomers. In contrast, when either (*S*) 1-naphthylamine (*S_C*)-**112** or (*R*) 2-naphthylamine (*R_C*)-**114** complexes were used, only 2 diastereomers are obtained. In addition, these two reactions exhibited the similar regioselectivity as the previous cycloaddition reaction involving diphenylvinylarsine as dienophile.

Scheme 2.7. [4+2] Diels-Alder Cycloaddition Reaction Involving Cy_2PhAs and DMPP

In this chapter, the synthesis of the new rigid asymmetric As-P bidentate ligand, having chirality on arsenic, via [4+2] Diels-Alder cycloaddition reaction will be reported. In addition, the stereoselectivity of chiral phenanthrylamine auxiliary in asymmetric [4+2] Diels-Alder synthesis of chiral As-P bidentate ligand will be reported.

2.2 Results and Discussion

2.2.1 [4+2] Diels-Alder Cycloaddition Reaction between diphenylvinylarsine and 5-phenyl-3,4-dimethylphosphole (DMPP) using (S) Bis(acetonitrile)[9-(1-(dimethylamino)ethyl-10-phenanthryl)-C,N]-palladium(II) perchlorate (*S_C*)-116 as chiral template

The [4+2] Diels-Alder cycloaddition reaction between diphenylvinylarsine and DMPP was conducted in the presence of a chiral palladium(II) template comprising a chiral *S* phenanthrylamine auxiliary. In this reaction, the bis-acetonitrile form of the (*S*) phenanthrylamine palladium(II) complex (*S_C*)-116 was used to induce [4+2] Diels-Alder reaction between diphenylvinylarsine **107** and DMPP **81** in dichloromethane at room temperature (Scheme 2.8). The reaction mixture was monitored using ³¹P NMR spectroscopy.

Scheme 2.8. [4+2] Diels-Alder Cycloaddition Reaction between diphenylvinylarsine and DMPP using the (*S*) phenanthrylamine palladium(II) complex

During the course of the reaction, intermediates were detected by ^{31}P NMR spectroscopy: i) intermediate **118**, from the signal δ 23.6, 15.0 $^2J_{\text{PP}}$ 42.0 Hz; ii) species **119**, from signal δ 13.8; iii) species **120** or **121**, from signal δ 69.0.

118 **119** **120** **121**

After overnight stirring, the phosphorus resonance signal pertaining to two product peaks at δ 117.3 and 118.3 had formed. The intermediates gradually disappear as the reaction progressed. The reaction was completed within 7 days. The ^{31}P NMR spectra of the products in solution exhibited two singlets at δ 117.2 and 118.3 at 5:1 ratio, respectively.

Separation of the diastereomeric products proved to be futile. Hence, the solution was treated with concentrated HCl solution to facilitate crystallization. It was observed that after treatment with HCl, the resulting dichloro product (R_P)-**79** exhibited only a single signal peak at δ 129.3 and easily crystallized as yellow prisms (0.58 g, 90 % yield) in dichloromethane and diethyl ether mixture: $[\alpha]_D -39.1$ (c 0.50, CH_2Cl_2). This dichloro complex is the same as the compound obtained by Aw⁴¹ *et al.* from the cycloaddition reaction using the chiral naphthylamine analogue of the palladium complex.

2.2.2 Regioisomerism of the Products

The resulting products complex (S_C,R_P)-**117a** and -**117b** are regioisomers. The major product δ 117.2 corresponds to the diastereomer (S_C,R_P)-**117a** since the less sterically hindered phosphabicyclo ring is *cis* to the sterically demanding NMe_2 group. On the other hand, the regioisomer (S_C,R_P)-**117b**, δ 118.3 is formed in minor amounts due to the less stable conformation brought about by the *cis* arrangement of the sterically demanding NMe_2 and tertiary arsine AsPh_2 groups. Formation of a single diastereomer after conversion to the dichloro complex confirms the theory of regioselectivity.

2.2.3 Single Crystal Diffraction Analysis of (R_P)-**79**

The molecular structure and absolute configuration of (R_P)-**79** was analyzed by single crystal X-ray diffraction analysis. The resulting data are identical to that previously reported by Aw and co-workers⁴¹. The molecular structure of the compound is shown in Figure 2.2.

Figure 2.2. Molecular structure and absolute configuration of (*R_P*)-79

2.2.4. Generation of Free Ligand, (*S_P*)-80

As illustrated in Scheme 2.9, treatment of the dichloromethane solution of (*R_P*)-79 with aqueous potassium cyanide liberates the optically active bidentate ligand (*S_P*)-80 as colorless oil in 86% isolated yield. The properties of this compound agrees well with the reported data by Aw *et al.*⁴¹

Scheme 2.9. Liberation of the optically pure bidentate ligand (S_P)-80

2.2.5 [4+2] Diels-Alder Cycloaddition between divinylphenylarsine and DMPP using (R) naphthylamine palladium(II) complex (R_C)-58

The first chiral rigid As-P bidentate ligand with chiralities on both arsenic and phosphorus atoms was synthesized. The reaction between divinylphenylarsine **122** and DMPP in dichloromethane at room temperature undergoes [4+2] cycloaddition in the presence of the chiral inducer (R) naphthylamine palladium(II) complex (R_C)-58 (Scheme 2.10).

Scheme 2.10. Chiral organopalladium(II) promoted [4+2] Diels-Alder Cycloaddition Reaction between divinylphenylarsine and DMPP

The reaction mixture was monitored by ^{31}P NMR spectroscopy and was found to be complete within 7 days. Two diastereomers were detected by ^{31}P NMR spectroscopy: δ 118.8 and 119.3 in 1:1.5 ratio, respectively.

Isolation of the diastereomers into optically pure forms by silica gel chromatography was futile. The two products could not be separated even in various combinations of solvents. Fractional crystallization appeared to cause decomposition

of the products as shown by the apparent change of color of the solution from yellow to black.

Hence, the crude solution of the products was directly treated with concentrated HCl to convert the complexes to their dichloro forms. This had facilitated its separation by fractional crystallization in dichloromethane and diethyl ether mixture. The less soluble, major diastereomer (S_P, S_{As})-**124** was isolated as light yellow square prisms with ^{31}P NMR resonance signal at δ 129.6 in CD_2Cl_2 : 30% yield, $[\alpha]_D +81.2$ (c 0.3, CH_2Cl_2). The more soluble diastereomer (S_P, R_{As})-**124** was obtained as orange rectangular solid with ^{31}P NMR δ 130.2 in the same solvent: 17% yield, $[\alpha]_D -3.4$ (c 0.3, CH_2Cl_2).

Normally, there will be two chirality centers on the phosphorus bridge however, in this case there is only one chirality on the phosphorus center.

It is noteworthy that no cycloaddition reaction between the vinyl arsines and DMPP occurred using the monodentate arsine **A** complex and phosphole. The ligands simply displace each other in the solution (Scheme 2.11). Equilibrium between the coordinated and free DMPP exists as shown by the ^{31}P NMR spectrum. The vinylarsine is not capable of acting as a dienophile without activation via coordination with the metal template.

Scheme 2.11. Ligand redistribution equilibrium between vinylarsines and DMPP

2.2.6 Single Crystal Diffraction Analysis of the Dichloro Complex (S_P,S_{As})-124

The molecular structure and absolute stereochemistry of the less soluble isomer (S_P,S_{As})-124 were determined by single crystal X-ray diffraction analysis. Figure 2.3 shows the ORTEP illustration of the molecule. Selected bond lengths and angles are listed in Table 2.1.

Figure 2.3. Molecular structure and absolute stereochemistry of (S_P,S_{As})-124

Table 2.1. Selected bond lengths (Å) and angles (°) for complex ($S_P S_{As}$)-124

Pd1-P1	2.237(1)	P1-Pd1-As1	83.2(2)
Pd1-As1	2.347(1)	P1-Pd1-Cl1	92.1(1)
Pd1-Cl1	2.350(1)	As1-Pd1-Cl1	173.3(1)
Pd1-Cl2	2.368(1)	P1-Pd1-Cl2	173.3(1)
As1-C15	1.920(3)	As1-Pd1-Cl2	91.6(2)
As1-C17	1.926(3)	Cl1-Pd1-Cl2	93.4(1)
As1-C1	1.958(2)	C15-As1-Cl7	104.7(1)
P1-C9	1.801(3)	C15-As1-Pd1	119.2(1)
P1-C3	1.849(2)	C17-As1-Pd1	115.8(1)
P1-C6	1.853(2)	C1-As1-Pd1	102.2(1)
C1-C2	1.554(3)	C3-P1-C6	80.9(1)
C1-C6	1.560(3)	C9-P1-Pd1	116.8(1)
C2-C3	1.559(3)	C3-P1-Pd1	119.6(1)
C3-C4	1.521(3)	C6-P1-Pd1	111.7(1)
C4-C5	1.328(4)	C4-C3-P1	101.8(2)
C5-C6	1.515(3)	C2-C3-P1	99.8(2)
C15-C16	1.288(4)	C5-C6-P1	102.6(2)
-	-	C1-C6-P1	96.5(1)

The molecular structure confirms the formation of the rigid As-P bidentate ligand with *S* absolute configuration on As, P and C(6) atoms and *R* for C(1) and C(3) atoms. The coordination geometry around palladium deviates slightly from planarity by having a small tetrahedral distortion. This is represented by having a non-zero

dihedral angle between the P(1)-Pd(1)-As(1) and Cl(1)-Pd(1)-Cl(2) planes in (*S_P*,*S_{As}*)-**124** of 6.2°. The angles As(1)-Pd(1)-Cl(1) and P(1)-Pd(1)-Cl(2) have the same value of 173.3(1)°. The angle Cl(1)-Pd(1)-Cl(2) [93.4(1)°] is slightly smaller than the corresponding angle [94.7(1)°] of the complex (*R_P*)-**79**. This is due to the steric effect by the vinyl group on the arsenic atom to the neighboring chloride ligand. Another manifestation of the bulkiness of the tertiary arsine moiety by the displacement of the phenyl by the vinyl group is the larger angle C(1)-As(1)-Pd(1) [102.2(1)°] compared to C(11)-As-Pd angle of 101.9(2)° of complex (*R_P*)-**79**. The P(1)-Pd(1)-As(1) angle [80.9(1)°] is consistent with the other bite angles of similar complexes consisting of a phophanorbornene moiety.

The Pd(1)-As(1) bond distance [2.35(1) Å] is noticeably longer than the Pd(1)-P(1) bond distance [2.24(1) Å]. This observation is true for most palladium(II) complexes containing bidentate arsine-phosphine ligands.^{41, 49} The Pd(1)-Cl(2) bond [2.37(1) Å] *trans* to phosphorus is slightly longer than that *trans* to arsenic [2.35(1) Å], representing the greater *trans* influence of the phosphorus atom. The newly formed bonds C(1)-C(6) and C(2)-C(3) have lengths consistent with a single carbon-carbon bond. The bond lengths of both C(4)-C(5) and C(15)-C(16) [1.33(1) Å and 1.29(1) Å respectively] are consistent of a double bond.

2.2.7 Liberation of the Free Ligand, (*R_P*,*R_{As}*)-**125**

Treatment of the dichloromethane solution of (*S_P*,*S_{As}*)-**124** with potassium cyanide facilitated the liberation of the optically pure bidentate ligand (*R_P*,*R_{As}*)-**125** as colorless oil in 90% isolated yield: $[\alpha]_D -43.7$ (*c* 2.3, CH₂Cl₂) (Scheme 2.12). Re-coordination of (*R_P*,*R_{As}*)-**125** with (*R_C*)-**58** re-generates (*S_P*,*S_{As}*)-**124**.

Scheme 2.12. Liberation of Chiral Bidentate (R_P, R_{As})-125

2.3 Conclusion

The chiral inducing effect of the relatively new chiral phenanthrylamine palladium(II) complex developed from our laboratory had shown comparative performance with the well-known naphthylamine palladium(II) complex over the stereoselective cycloaddition reaction between diphenylvinylarsine and DMPP. Only one enantiomeric form of the chiral bidentate ligand (S_P)-80 was obtained from the reaction although the presence of regioisomers in the diastereomeric complexes was detected. This rigid chiral arsine ligand has initially been reported by our group.⁴¹

The study was successfully extended to the preparation of enantiomerically pure As-P bidentate ligand carrying a stereogenic center on arsenic. A mixture of diastereomers consisting of chiral bidentate ligands enantiomeric on arsenic was obtained. However, the stereoselectivity of the diastereomers produced is not satisfactory wherein an almost equal ratio was obtained. The presence of a bulky group on the naphthalenic carbon *ortho* with the metalated carbon could possibly improve the selectivity of this reaction.

2.4 Experimental Section

2.4.1 Instrumentation

Air-sensitive manipulations were carried out using Schlenk and cannula techniques under a positive pressure of argon. NMR spectra were recorded at 25 °C on Bruker ACF 300 and 500 MHz spectrometers. Optical rotations were measured on the specified solution in a 1 dm cell at 25 °C with a Perkin-Elmer Model 341 polarimeter. Elemental Analyses were performed by the Elemental Analysis Laboratory of the Division of Chemical and Biological Sciences of Nanyang Technological University. All melting points were measured using the SRS Optimelt Automated Melting Point System, SRS MPA100.

2.4.2 Reagents

All solvents used for synthesis of ligands and reactions were deoxygenated using a positive pressure of argon. Analytical grade chemicals were purchased from Sigma-Aldrich and Strem Chemicals. The chiral palladium complexes bis(μ -chloro)bis[(*R/S*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*]dipalladium(II) (*S_C/R_C*)-**58**⁵⁰, bis(acetonitrile)[(*S*)-9-(1-(dimethylamino)ethyl-10-phenanthrenyl)-*C,N*]palladium(II) perchlorate (*S_C*)-**116**⁵¹, and 1-phenyl-3,4-dimethylphosphole⁵² were prepared according to literature methods.

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

2.4.3 Syntheses

Preparation of diphenylvinylarsine

To a stirred solution of diphenylarsine (9.00 g, 39.1 mmol) in dry THF was added flattened sodium metal (1.80 g, 78.2 mmol). The solution was stirred at room temperature for 16 hours in which time the solution turned from colorless to red. This reaction mixture was then added slowly to a cooled solution of vinylbromide (4.18 g, 39.1 mmol) in THF at -96 °C. The reaction was allowed to reach ambient temperature overnight with continuous stirring. After reducing the solvent to half the original volume, the mixture was hydrolyzed by saturated ammonium chloride solution and extracted by diethyl ether. The organic layer was separated and dried over magnesium sulfate. The solvent was removed and the residue was distilled under reduced pressure to give diphenylvinylarsine as colorless oil: 8.12 g (81% yield), bp 118-130 (0.2 mmHg). ^1H NMR (CDCl_3): δ 5.64 (dd, 1H, $^2J_{\text{H-H}}=18.0$ Hz, $^2J_{\text{H-H}}=1.7$ Hz, $\text{AsCH=CHH}'$ (*trans*)), 6.00 (dd, 1H, $^3J_{\text{H-H}}=11.0$ Hz, $^3J_{\text{H-H}}=1.6$ Hz, $\text{AsCH=CHH}'$), 6.73 (dd, 1H, $^2J_{\text{H-H}}=19.0$ Hz, $^3J_{\text{H-H}}=11.0$ Hz, $\text{AsCH=CHH}'$ (*cis*)), 7.14-7.36 (m, 10H, aromatics)

Preparation of phenyldichloroarsine

The phenyldichloroarsine ligand was prepared based on the modification of the procedure in the literature⁵³. The phenylarsonic acid (25.00 g, 123.7 mmol) was dissolved in concentrated HCl (150 mL). The solution was then transferred to a dropping funnel. Iodine (0.17 g, 1.3 mmol) was then added to the solution mixture.

Sulfur dioxide gas was bubbled into the solution for a period of 2 hours. The deep red layer at the bottom of the funnel was then collected into the Schlenk flask and dried over 4A molecular sieves overnight. The solution was transferred into another flask for distillation. The phenyldichloroarsine was obtained as colorless oil: 22.96 g (83% yield), bp 82-90 °C (0.8 mmHg), ^1H NMR (CDCl_3 , 300 MHz): δ 7.53-7.89 (m, 5H, aromatics).

Preparation of phenyldivinylarsine

This ligand was prepared in a similar procedure used in the preparation of its phosphine analogue based on the literature.⁵⁴ A solution of vinylbromide (6.00 g, 55.0 mmol) in dry THF was slowly added to magnesium turnings (2.40 g, 100.0 mmol) in THF (100 mL). The reaction mixture was stirred and refluxed for a period of 1 hour. Upon cooling to room temperature, the Grignard reagent was slowly added to a cooled solution of dichlorophenylarsine (4.40 g, 20.0 mmol) in THF (100 mL) at -96 °C. The reaction was allowed to reach ambient temperature overnight. The solvent was removed and the residue was treated with saturated solution of ammonium chloride followed by extraction by diethyl ether. The organic layer was separated and dried over magnesium sulfate. The solvent was removed and the residue was distilled under reduced pressure to isolate phenyldivinylarsine as colorless oil: 3.09 g (75% yield), bp 58-61 °C (0.2 mmHg). ^1H NMR (CDCl_3): δ 5.66 (dd, 1H, $^2J_{\text{H-H}}=19.0$ Hz, $^3J_{\text{H-H}}=1.6$ Hz, $\text{AsCH=CHH}'$ (*trans*)), 5.93 (dd, 1H, $^3J_{\text{H-H}}=11.0$ Hz, $^3J_{\text{H-H}}=1.6$ Hz, $\text{AsCH=CHH}'$), 6.57 (dd, 1H, $^2J_{\text{H-H}}=19.0$ Hz, $^3J_{\text{H-H}}=11.0$ Hz, $\text{AsCH=CHH}'$ (*cis*)), 7.16-7.41 (m, 5H, aromatics)

Isolation of dichloro- $\{[1\alpha,4\alpha,5\alpha(S),7R]-[5-(diphenylarsino)-2,3-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-2-ene-As^5,P^7]\}$ palladium(II) (R_P)-79.

The bis-acetonitrile(phenanthryl) palladium complex (S_C)-**116**⁵¹ (0.56 g, 1.0 mmol) in dichloromethane (150 mL) was reacted with the mixture of DMPP (0.20 g, 1.0 mmol) and diphenylvinylarsine (0.27 g, 1.0 mmol) in dichloromethane (100 mL). The reaction mixture was stirred at room temperature and monitored using ^{31}P NMR spectroscopy. After 3 days of stirring the ^{31}P NMR shows the intensity of the intermediates had largely reduced to almost zero while the two diastereomeric products were observably developed. The reaction was left in stirring for the next 3-4 days until all the intermediates were converted to products. The ^{31}P NMR signals (121 MHz, CDCl_3) of the two diastereomeric products was observed at 117.21 (s) and 118.31 (s) ppm in 5 is to 1 ratio.

The solvent of the crude product was reduced to 50 mL and subsequently converted to its dichloride form by treatment with concentrated HCl solution (30 mL) overnight at room temperature. The organic layer was separated and washed with deionized water (3×50 mL) followed by drying over MgSO_4 . The product, (R_P)-**79** was crystallized as yellow prisms using dichloromethane and diethyl ether as solvents: 0.58 g (90 % yield), $[\alpha]_D -39.1^\circ$ (c 0.50, CH_2Cl_2), mp $> 250^\circ\text{C}$ (dec). Calcd. for $\text{C}_{26}\text{H}_{26}\text{AsPPdCl}_2$ C 50.2, H 4.2 found C 49.9 H 4.1. The ^{31}P NMR (121 MHz, CD_2Cl_2) shows a single resonance signal 129.42 (s) ppm. ^1H NMR (300 MHz): δ 1.48 (s, 3H, $\text{C}=\text{CMe}$), 1.60 (s, 3H, $\text{C}=\text{CMe}$), 1.94 (ddd, 1H, $^3J_{\text{H-P}}=24.5$ Hz, $^2J_{\text{H-H}}=14.5$ Hz, $^3J_{\text{H-H}}=9.2$ Hz, $H_{\delta,endo}$), 2.49 (d, 1H, $^2J_{\text{H-H}}=14.5$ Hz, $H_{\delta,exo}$), 3.04 (dd, 1H, $^3J_{\text{H-P}}=44.8$ Hz, $^3J_{\text{H-H}}=9.2$ Hz, H_5), 3.08 (s, 1H, H_I), 3.44 (s, 1H, H_4), 7.39-8.06 (m, 15H, aromatics).

Generation of (1 α ,4 α ,5 α (S),7S)-[5-(diphenylarsino)-2,3-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-2-ene-As⁵,P⁷] (S_P)-80

A solution of (R_P)-**79** (0.44 g, 0.7 mmol) in dichloromethane was treated with aqueous solution of potassium cyanide (1.00 g) for 30 min. The resultant colorless organic layer was separated and washed thoroughly with water. This was then dried using anhydrous magnesium sulfate. The solvent was then removed to give the colorless oil: 0.27 g (86 % yield).

Synthesis of dichloro-{[1 α ,3 α (R),6 α (S),7S,5S]-[5-(phenylvinylarsino)-2,3-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-2-ene-As⁵,P⁷]}palladium(II) (S_P,S_{As})-124.

The naphthyl palladium(II) dimer (R_C)-**58** (1.65 g, 2.4 mmol) was reacted with divinylphenylarsine (1.00 g, 4.8 mmol) in dichloromethane for 30 mins. The monodentate complex was immediately treated with silver perchlorate (1.00 g, 4.8 mmol) in water. The silver chloride was filtered out and the solution extracted and dried over MgSO₄. This ionic metal salt was treated with 1-phenyl-3,4-dimethylphosphole in dichloromethane at room temperature. The reaction mixture was monitored by ³¹P NMR spectroscopy and was found to be complete in 7 days. The crude product consisted of two diastereomers with ³¹P NMR δ 118.8 and 119.3 in almost equal ratios. The crude product solution was treated with concentrated HCl solution to convert the complex to its dichloro form and to facilitate its crystallization. The two diastereomeric dichloro complexes were isolated by fractional crystallization

in dichloromethane and diethyl ether solution. The less soluble isomer (S_{AS}, S_P)-**124** was isolated as light yellow square prisms: 0.82 g (30% yield), $[\alpha]_D +81.2$ (c 0.3, CH_2Cl_2) mp >200 °C (dec) Anal. Calcd. for $\text{C}_{22}\text{H}_{24}\text{AsPPdCl}_2$: C, 46.2; H, 4.2. Found: C, 45.9; H, 4.1. ^{31}P NMR (CD_2Cl_2 , 121 MHz): δ 129.6 (s). ^1H NMR (CD_2Cl_2 , 500 MHz): δ 1.45 (s, 3H, $\text{C}=\text{CMe}$), 1.62 (s, 3H, $\text{C}=\text{CMe}$), 2.05 (ddd, 1H, $^3J_{\text{P-H}}=23.5$, $^2J_{\text{H-H}}=14.0$, $^3J_{\text{H-H}}=8.5$ Hz, $H_{6,\text{endo}}$), 2.58 (d, 1H, $^2J_{\text{H-H}}=12.0$ Hz, $H_{6,\text{exo}}$), 2.84 (dd, 1H, $^3J_{\text{P-H}}=46.0$, $^3J_{\text{H-H}}=9.0$ Hz, H_5), 2.94 (s, 1H, H_1), 3.47 (s, 1H, H_4), 6.39 (d, 1H, $^2J_{\text{H-H}}=18.0$ Hz, $\text{AsCHCHH}_{\text{trans}}$), 6.42 (d, 1H, $^3J_{\text{H-H}}=11.0$ Hz, AsCHCHH), 6.77 (dd, 1H, $^2J_{\text{H-H}}=18.0$, $^3J_{\text{H-H}}=11.0$ Hz, $\text{AsCHCH}_{\text{cis}}\text{H}$), 7.42-7.80 (m, 10H, aromatics). On the other hand, the more soluble isomer (R_{AS}, S_P)-**124** was obtained as orange prisms: 0.48 g (17% yield) $[\alpha]_D -3.4$ (c 0.3, CH_2Cl_2) mp >200 °C (dec). ^{31}P NMR (CD_2Cl_2 , 121 MHz): δ 130.2 (s). ^1H NMR (CD_2Cl_2 , 500 MHz): δ 1.59 (s, 3H, $\text{C}=\text{CMe}$), 1.63 (s, 3H, $\text{C}=\text{CMe}$), 1.87 (ddd, 1H, $^3J_{\text{P-H}}=24.0$, $^2J_{\text{H-H}}=14.5$, $^3J_{\text{H-H}}=9.2$ Hz, $H_{6,\text{endo}}$), 2.33 (d, 1H, $^2J_{\text{H-H}}=12.5$ Hz, $H_{6,\text{exo}}$), 2.85 (dd, 1H, $^3J_{\text{P-H}}=46.2$, $^3J_{\text{H-H}}=9.2$ Hz, H_5), 3.26 (s, 1H, H_1), 3.44 (s, 1H, H_4), 6.50 (d, 1H, $^2J_{\text{H-H}}=11.0$ Hz, AsCHCHH), 6.57 (d, 1H, $^3J_{\text{H-H}}=18.0$ Hz, $\text{AsCHCHH}_{\text{trans}}$), 6.69 (dd, 1H, $^2J_{\text{H-H}}=18.0$, $^3J_{\text{H-H}}=11.0$ Hz, $\text{AsCHCH}_{\text{cis}}\text{H}$), 7.50-8.12 (m, 10H, aromatics).

Generation of (1 α ,3 α (R),6 α (S),7 R ,5 R)-[5-(phenylvinylarsino)-2,3-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-2-ene- As^5, P^7]-(R_P, R_{AS})-125****

A solution of (S_{AS}, S_P)-**124** (0.03 g, 0.05 mmol) in dichloromethane was treated with aqueous solution of potassium cyanide (1.00 g) for 30 min. The resultant colorless organic layer was separated and washed thoroughly with water. This was

then dried using anhydrous magnesium sulfate. the solvent was then removed to give the colorless oil: 0.02 g (90 % yield), ^{31}P NMR (CDCl_3 , 121 MHz): δ 96.0.

Crystal Structure Determination

Crystal data and summary of the crystallographic analyses are given in the appendix. Diffraction data were collected at the Nanyang Technological University using Bruker Kappa Apex II CCD diffractometer with Mo-K α radiation (graphite monochromator) using θ and ω -scans. All non-hydrogen atoms were refined anisotropically while hydrogen atoms were introduced at a fixed distance from the carbon and were assigned fixed thermal parameters. The absolute configurations of the chiral complexes were determined unambiguously using the Flack parameter.⁵⁵

CHAPTER 3

Alkynylarsine Insertion Reaction into Aryl C-Pd bond

3.1 Introduction

Insertion reactions between cyclo-metalated compounds and unsaturated molecules had long been regarded as convenient synthetic routes for some heterocyclic⁵⁶ and polycyclic⁵⁷ organic compounds as well as new types of metallocycles^{58, 59}. The CO insertion reaction provides a simplistic way of functionalizing alkyl⁶⁰ or aryl⁶¹ bond by formation of carbonyl groups. Such a reaction provides important intermediates in organic syntheses. In addition, this reaction has its applicability in the industrial process such as the polymerization of olefins.⁶²

In 1955, the synthesis of the heterocyclic derivative of isoindolinone via cobalt complex-catalyzed reaction was reported.⁶³ In this reaction, the *N*-benzylideneaniline **126** was reacted with carbon monoxide in the presence of a catalytic amount of octacarbonyl di-cobalt complex to yield 2-phenylisoindolin-1-one **127** (Scheme 3.1).

Scheme 3.1. Cobalt complex-catalyzed insertion of CO in Co-C bond

Similarly, by the reaction between the 1,2-diphenyldiazene **128** and carbon monoxide was facilitated by using the same catalyst $[\text{Co}(\text{CO})_4]_2$ for the formation of **129** (2-phenyl-1,2-dihydrocinnoline-3,4-dione) a quinazolinedione derivative (Scheme 3.2).⁶⁴

Scheme 3.2. Double insertion of CO into Co-C bond

In the late 1960's, it was proposed that complex **130** could be the intermediate in this type of reaction, where an *ortho*-metalated aryl group of the substrate comprising of a metal-carbon covalent bond and coordinated to the nitrogen donor atom form a 5-membered organometallic ring.^{56, 65} The nickel⁶⁶, platinum⁶⁷ and palladium⁶⁷ analogues of **130** were prepared and all exhibited similar reactivity in metalation on the carbon in the *ortho* position relative to the donor atom of the aryl group. The insertion of 1 mole of carbon monoxide was similarly observed in the palladium(II) analogue forming the same isoindolinone product **127** from the cobalt complex.⁶⁸

At present, studies on *ortho*-metalated complexes are increasingly important especially in the area of organic synthesis due to the reactivity of the σ metal-carbon (M-C) bond towards various alkenes, alkynes, carbon monoxide and isocyanide reagents. Particularly, the insertion of alkenes in various organometallic palladacycles has become

one of the most important C-C coupling reactions forming various derivatives of aryl olefins⁶⁹ and its wide applicability in Heck reactions^{70,71}

Insertion reactions of di-substituted alkynes in σ M-C bond of various cyclo-metalated complexes have been reported. (M=Ru⁷², Rh⁷³, Co^{65,74}, Pd^{58,59,75-77}). The group of Dehand⁵⁸ first reported the insertion reaction of derivatives of acetylene in cyclo-palladated complexes. In this earlier work, only the bis-insertion products of di-substituted acetylenes were obtained for both cyclo-palladated derivatives of dimethylbenzylamine **131** and 8-methylquinoline **133** (Scheme 3.3). It is noteworthy that there is no single insertion of the alkyne derivatives observed even after addition of less than 1 equivalence of the acetylene derivatives.

Scheme 3.3. Bis-insertion of derivatives of acetylene in Pd-C bonds of various organopalladium(II) complexes

Recently, our group studied the insertion reactions of phosphino alkynes in various cyclopalladated(II) and –platinated(II) complexes.⁷⁸ The study highlighted three important aspects: (a) the *ortho*-palladated complex of naphthylamine (*S_C*)-**58** was not reactive towards phosphino alkyne insertion (Scheme 3.4), (b) cycloplatinated complexes of both phenyl- (*S_C*)-**137** and naphthylamine (*S_C*)-**138** derivatives were unreactive towards insertion reaction (Scheme 3.5), and (c) a stoichiometric ratio of 1:0.5 between the coordinated alkynyl phosphine and the cyclo-palladated dimer, respectively, was necessary.

Scheme 3.4. Insertion reaction between palladium complex-activated phosphinoalkyne (*S_C*)-135 and naphthylamine palladium complex (*S_C*)-58

Scheme 3.5. Insertion reaction between activated phosphinoalkyne (S_C)-135 and various organoplatinated(II) complex (S_C)-137/138

The products of the reactions in Scheme 3.4 and 3.5 have instead showed that the alkynyl phosphine had migrated from the *ortho*-palladated phenylamine (S_C)-135 complex to the *ortho*-palladated naphthylamine (S_C)-58 or *ortho*-platinated complexes (S_C)-137/138, resulting to the insertion of the C-C triple bond of the alkynyl phosphine into the Pd-C bond of the cyclo-palladated phenylamine complex, (S_C,S_C)-141-143.

(S_C, S_C)-141

(S_C, S_C)-142

(S_C, S_C)-143

It appears that, the alkynyl phosphine needs to be coordinated to the palladium(II) or platinum(II) complex to activate the C-C triple bond. The acryl C-Pt bonds are unreactive towards insertion reaction. It is believed that the reaction proceeds via the bridge splitting at the chloride ligand bridging the dimer with concomitant coordination of the C-C triple bond to the metal. This η^2 -coordination of the alkyne enhances its nucleophilicity hence, enhancing its reactivity. The mechanism of the insertion reaction was postulated to proceed via a four-centered transition state wherein the reaction involves the concerted bond breakage of σ M-C_{aromatic} bond and the C-C triple π bond and the bond formation of a new M-C and C-C σ bonds **144**, the metal attaches to the carbon nearest to the phosphorus donor atom.

144

The analogous arsino alkyne insertion in the cyclopalladated complex has not been reported hitherto. The work that will be discussed in this chapter deals with the insertion of coordinated alkynyl arsine in the *ortho*-palladated phenyl amine complex.

3.2 Results and Discussion

3.2.1 Preparation of Diphenyl-1-propynylarsine, **148**

The preparation of diphenyl-1-propynylarsine is outlined in Scheme 3.6 below. Initially, diphenylchloroarsine is prepared by heating diphenylarsine and chloroacetic acid at 160 °C.⁷⁹ The resulting diphenylchloroarsine was treated with an excess amount of propynylmagnesiumbromide in tetrahydrofuran at reduced temperature to obtain the alkynyl arsine.

Scheme 3.6. Synthetic route for the preparation of diphenyl-1-propynylarsine

3.2.2 Insertion of Alkynylarsine in Pd-C Bond

The diphenyl-1-propynylarsine **148** was first reacted with the chiral dimeric platinum complex (*R_C*)-**138** in dichloromethane for *ca* 1 hour at room temperature (Scheme 3.7). The resulting complex solution was treated with half mole of the achiral dimeric palladium complex **131** in the same solvent at room temperature. The reaction was

completed after *ca* 5 days. The product was isolated through silica gel chromatography using ethyl acetate-hexane mixture as eluent. The slow addition of diethyl ether to the purified fraction in CH_2Cl_2 resulted in the formation of yellow-orange rectangular prisms: yield 0.21 g (56% yield), $[\alpha]_{\text{D}} +184$ (c 0.1, CH_2Cl_2).

Scheme 3.7. Synthetic route for the insertion of diphenyl-1-propynylarsine into Pd-C bond of 131 forming the hetero-metallocyclic $(R_C)\text{-150}$

3.2.3 X-ray Crystal Diffraction Analysis of $(R_C)\text{-150}$

The molecular structure and absolute configuration of the heterocyclic complex $(R_C)\text{-150}$ were determined by single crystal X-ray diffraction analysis. The ORTEP illustration of the molecule is shown in Figure 3.1 while selected bond lengths and angles are shown in Table 3.1. The X-ray structural analysis of the insertion product revealed that the desired μ -chloro hetero-nuclear complex has been formed wherein the alkynyl moiety of the arsine ligand was inserted into the Pd-C bond of the achiral dimethylbenzylamine palladium complex.

Figure 3.1. Molecular structure and absolute configuration of the hetero-nuclear complex (R_C)-150

Table 3.1. Selected bond lengths (Å) and angles (°) for complex (*R_C*)-150

Pt1-Cl1	1.989(5)	Cl1-Pt1-N1	80.7(2)
Pt1-N1	2.124(4)	N1-Pt1-Cl1	94.0(1)
Pt1-Cl1	2.413(1)	Cl1-Pt1-As1	98.8(1)
Pt1-As1	2.347(1)	N1-Pt1-As1	176.1(1)
As1-C15	1.959(5)	Cl1-Pt1-As1	86.6(1)
As1-C21	1.953(5)	C27-Pd1-N2	93.4(2)
As1-C27	1.954(4)	C27-Pd1-Cl2	168.9(1)
Pd1-C27	1.990(5)	N2-Pd1-Cl2	91.3(1)
Pd1-N2	2.104(4)	C27-Pd1-Cl1	85.5(1)
Pd1-Cl1	2.354(1)	Pd1-Cl1-Pt1	88.5(1)

Pd1-Cl2	2.449(2)	C27-As1-Pt1	108.3(1)
C27-C28	1.343(6)	As1-C27-C28	128.3(4)
C28-C29	1.506(7)	C27-C28-C30	119.7(5)
C28-C30	1.493(7)	Pd1-C27-C28	129.4(4)
N2-C36	1.497(7)	N2-C36-C35	113.1(4)
C35-C36	1.506(7)	Pd1-N2-C36	115.7(3)

The 7-membered ring adopts a pseudo-boat conformation (Figure 3.1). The same conformation was observed in similar insertion products involving the palladium complex.^{59, 78, 80, 81} The distance between the C=C bond C(27)-C(28) [1.34(1)Å] and the geometry around the olefinic carbons are within the values of similar complexes derived from insertion of alkynylphosphines⁷⁸. However, some angles within the 7-membered ring of the complex have larger value than the corresponding angles of mono-nuclear complexes of palladium^{59, 80, 81}. The angles Pd(1)-C(27)-C(28) [129.4(4)°] and As(1)-C(27)-C(28) [128.3(4)°] are exceptionally large. The 5-membered ring, on the other hand, consisting of the platinum and palladium metal centers adopts an envelope conformation. One unique feature of this structure is the long range bond between Pd(1) and As(1) [3.07(0)Å] forming a 5 coordination palladium center.

3.2.4 ¹H NMR Spectroscopic Analysis of the Organoplatinum(II) complex, (*R_C*)- 150

This chiral organoplatinum complex (*R_C*)-**138** is known to undergo *cis-trans* regioisomeric equilibrium as a result of the facile bridge-splitting reaction between the two platinum centers in solution (Scheme 3.8).⁷⁸ Similar regioisomerism was reported

by the group of Wild⁸² with the analogous palladium complex. After the coordination of the arsine ligand to form the monomeric complex (*R_C*)-**150** these signals simplified into two signals one from each diastereotopic Me group. The signal from the proton on the stereogenic carbon had also simplified from a quintet, due to the average signals from the *cis-trans* isomers, into a quartet.

Scheme 3.8. *Cis-trans* regioisomerism of the platinum complex (*R_C*)-**138** in solution

Before the insertion reaction, the ¹H NMR resonance signals corresponding to NMe₂ of the dimethylbenzylamine complex **131** almost overlap with each other while

that of the CH₂ group gave a singlet. After insertion, the ¹H NMR spectrum of the product (*R_C*)-**150** shows that these signals became well-defined individual singlets. Accordingly, these Me groups are diastereotopic, due to the presence of the chiral carbon center in the naphthylamine auxiliary (Scheme 3.9).

Scheme 3.9. Diastereotopic nature of NMe₂ and CH₂ groups of the dimethylbenzylamine auxiliary in (*R_C*)-**150**

3.2.5 Assignments of ¹H NMR Resonance Signals of (*R_C*)-**150**: Two-dimensional ¹H-¹H ROESY NMR Spectroscopy Analysis

The assignments of ¹H NMR resonance signals for the hetero-nuclear complex (*R_C*)-**150** in CDCl₃ were derived from the analysis of its 2D-ROESY NMR spectrum. The ROESY NMR spectrum of (*R_C*)-**150** in the same solvent is shown in Figure 3.2.

Figure 3.2. 2D-ROESY NMR of (R_C) -150 in $CDCl_3$. Selected NOE Interactions:
A: $Me_{38}-H_{36}$, B: $Me_{38}-Me_{37}$, C: $H'_{36}-Me_{38}$, D: $Me_{12}-Me_{14}$, E: $H_{36}-H'_{36}$, F: $Me_{13}-Me_{14}$, G: $Me_{12}-H_{11}$, H: $Me_{13}-H_{11}$, I: $Me_{14}-H_{11}$, J: $H_{34}-H_{36}$, K: $H_{34}-Me_{37}$, L: $Me_{29}-H_{31}$, M: $Me_{12}-H_8$, N: $Me_{29}-o-Ph_{As}$, O: $Me_{38}-o-Ph_{As}$, P: $Me_{12}-o-Ph_{As}$, Q: $H'_{36}-o-Ph_{As}$, R: $H_{11}-H_8$, ●: H_2O , ■: CH_2Cl_2 , ◆: $CHCl_3$

Similar to the 2D- ^1H - ^1H ROESY NMR analysis of other analogous organometallic complexes⁸³ comprising of the 5-membered *ortho*-metalated dimethyl[(*S/R*)-1-(1-naphthyl)ethyl] amine auxiliary, the 5-membered organo-platinum(II) complex moiety of (*R_C*)-**150** is locked in a stable conformation defined by a set of characteristic NOE patterns: NOE signals (G-I) are observed due to the interactions of H(11) with Me(12)-Me(14), the very strong interaction between this proton and H(8) of the aromatic ring (R) indicates the close proximity of these protons with each other while the weaker signal (M) shows that the methyl group on the stereogenic carbon Me(12) exclusively adopts the axial position locking the 5-membered organometallic ring in a stable δ conformation (Figure 3.3). There is no signal showing any interaction between this methyl group and the axially oriented Me(13) on nitrogen, only its interaction with the equatorial methyl group Me(14) of nitrogen was observed (D).

Figure 3.3. (a) Dreiding model of the 5-membered ring conformation of platinum(II) complex, (b) Newmann projection along C(11) and N

The strong signals corresponding to N and Q represent the interactions of the *ortho* protons of the phenyl groups on arsenic with Me(29) and H'(36) respectively. These signals confirm two points: (i) the *cis* orientation of Me(29) with respect to arsine and

(ii) the boat conformation of the 7-membered ring wherein C(36) is close to the arsine moiety (Figure 3.4).

Figure 3.4. Boat conformation of the 7-membered ring

Due to the proximity of Me(37) with the aromatic proton H(34) of the benzyl group when the 7-membered ring is in boat conformation, the strong signal K is manifested. Similarly, signal J representing the interaction between H(36) and H(34) displays strong intensity due to their proximity. Finally, signal B represents the interaction between the geminal Me(37) and Me(38), their ^1H NMR chemical shifts differ by about 0.60 ppm. This confirms the previous statement that the two methyl groups of the original dimethylbenzylamine had become diastereotopic after the insertion reaction.

3.3 Conclusion

The insertion between the metal complex activated alkynylarsine and achiral organopalladium(II) complex was successfully demonstrated. This facile reaction was conducted at ambient condition in dichloromethane to give an almost quantitative yield of the hetero-bimetallic complex (R_C)-**150**. The reaction was monitored by ^1H NMR spectroscopy. The C-C triple bond of the alkynylarsine is activated by the organoplatinum complex while the As-C bond remains stable. The insertion reaction is useful in providing insight to the mechanism of transition metal complex mediated reactions involving the formation of new C-C bonds.

3.4 Experimental Section

3.4.1 Instrumentation

Please refer to Section 2.4.1.

3.4.2 Reagents

All solvents used for synthesis of ligands and reactions were deoxygenated using a positive pressure of argon. Analytical grade chemicals were purchased from Sigma-Aldrich and Strem Chemicals. The chiral palladium complex di- μ -chloro-bis[*N,N*-dimethylbenzylamine- C^2,N]dipalladium(II) **131**⁸⁴ was prepared according to literature methods while the chiral metal complex di- μ -chloro-bis[(*R*)-1-[1-(dimethylamino)ethyl]naphthyl- C^2,N]diplatinum(II) (*R_C*)-**138**⁸⁵ was prepared based on the procedure in literature using the *R* handform of the amine.

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

3.4.3 Syntheses

Preparation of diphenylchloroarsine **147**

This ligand was prepared based on the modification of literature procedure⁷⁹. A mixture of diphenylarsine (0.52 g, 2.3 mmol) and chloroacetic acid (0.32 g, 3.4

mmol) was gradually heated to 160 °C. During the initial stage of heating, evolution of HCl was observed. The reaction mixture was left stirring for 1 hour at 160 °C, after which it was allowed to be cooled to room temperature. It was subsequently dissolved in petroleum ether and then cooled over an ice bath. It was left for 30 minutes until the oil separated from the petroleum solution. The solution was decanted and the solvent removed under vacuo. Diphenylchloroarsine ligand was obtained as a colorless viscous oil: 0.47 g (78% yield). ¹H NMR (300 MHz, CDCl₃): δ 7.43-7.66 (m, 10H, aromatics)

Preparation of 1-propynyldiphenylarsine 148

Diphenylchloroarsine (0.46 g, 1.7 mmol) **147** was dissolved in dry THF and cooled to -78 °C. This was then treated with 1-propynylmagnesiumbromide (4.92 g, 2.6 mmol) in THF. The mixture was left stirring and allowed to reach ambient temperature overnight. The solvent was removed and the residue treated with a saturated ammonium chloride solution. The product was extracted using diethyl ether and the organic layer separated and dried over magnesium sulfate. The solvent was removed completely to give the 1-propynyldiphenylarsine as air-stable yellow oil: 0.45 g (96% yield). ¹H NMR (300 MHz, CDCl₃): δ 2.08 (s, 3H, Me), 7.30-7.68 (m, 10H, aromatics).

Synthesis of μ -chloro $\{ \{R-1-[1-(\text{dimethylamino})\text{ethyl}]\text{naphthyl-}C^2,N\} \text{ platinum(II) } \{1-[(\text{dimethylamino})-2-(E)-1-(\text{diphenylphosphino})\text{prop-1-en-2-yl-}C^4]\text{benzyl-}N\} \text{ chloro palladium(II), } (R_C)\text{-150}$

1-propynyldiphenylarsine (0.13 g, 0.4 mmol) was dissolved in dichloromethane and into this (R_C)-**138** (0.16 g, 0.2 mmol) was added. The reaction mixture was stirred for 1 hour at room temperature. The achiral palladium(II) complex **131** (0.10 g, 0.2 mmol) was then added into the solution. The insertion reaction was completed within 5 days by monitoring the disappearance of the free ligand peak in the ^1H NMR spectrum. The crude product was purified by silica gel chromatography using ethyl acetate-hexane as eluent. The isolated pure product was subsequently re-crystallized in a solution of dichloromethane and diethyl ether. The insertion product was obtained as yellow-orange rectangular crystals: 0.20 g (56% yield), $[\alpha]_D +199.0$ (c 10.0, CH_2Cl_2), mp 205-208 °C (dec). Anal. Calcd. for $\text{C}_{38}\text{H}_{41}\text{AsPdPtCl}_2\text{N}_2 \cdot \text{CH}_2\text{Cl}_2$: C, 44.3; H, 4.1; N, 2.6 Found: C, 44.2; H, 4.5; N, 2.7. ^1H NMR (CDCl_3 , 300 MHz): δ 1.88 (s, 3H, Me_{29}), 1.99 (s, 3H, Me_{38}), 2.21 (dd, 3H, $^3J_{\text{H-H}}=6.3$ Hz, Me_{12}), 2.47 (d, 1H, $^2J_{\text{H-H}}=11.1$ Hz, H_{36}), 2.62 (s, 3H, Me_{37}), 2.75 (s, 3H, Me_{13}), 3.34 (d, 1H, $^2J_{\text{H-H}}=11.1$ Hz, H_{36}), 3.36 (s, 3H, Me_{14}), 4.54 (qt, 1H, $^3J_{\text{H-H}}=6.3$ Hz, H_{11}), 6.80 (d, 1H, $^3J_{\text{H-H}}=8.4$ Hz, H_2), 7.00 (d, 1H, $^3J_{\text{H-H}}=8.4$ Hz, H_3), 7.07 (d, 1H, $^3J_{\text{H-H}}=7.5$ Hz, H_{34}), 7.18-7.66 (m, 12H, aromatics), 7.72 (d, $^3J_{\text{H-H}}=8.1$ Hz, H_8), 7.88-7.98 (m, 4H, $o\text{-Ph}_{\text{As}}$).

Crystal Structure Determination

Please refer to the Crystal structure determination of Chapter 2.

CHAPTER 4

Asymmetric Hydroarsination Reaction

4.1 Introduction

Asymmetric addition reaction between an E-H (*i.e.* E = N, P) moiety of an amine or phosphine and a C-C double bond of an unsaturated compound is one of the most important reactions in producing nitrogen or phosphorus containing chiral compounds (Scheme 4.1).^{86, 87} As early as 1961, Stern and Spector investigated the addition reaction involving nitrogen-hydrogen using palladium(II) complexes as catalysts.⁸⁸ However, it is only until recently that these reactions are being applied to asymmetric synthesis of chiral molecules.⁴⁻⁶ Organometallic reagents comprising transition metals and chiral auxiliaries have been reported to be able to promote these reactions efficiently.⁸⁹⁻⁹⁵

Scheme 4.1

Reports on metal ion promoted asymmetric hydroamination have shown that it may proceed in two different pathways. The first pathway involves the oxidative addition of the N-H bond onto the metal ion followed by insertion of the olefin and finally reductive elimination of the chiral product.⁹⁶ The second pathway involves a nucleophilic reaction between a coordinated olefin on the chiral metal promoter and the free amine followed by protonolysis to release the final product.^{90, 97} There are also reports on intramolecular asymmetric hydroamination of amino-olefins forming chiral pyrrolidines and piperidines using chiral organolanthanide complexes.^{98, 99} Recently, we have reported the asymmetric synthesis of a P-chiral iminophosphine *via* the metal ion promoted asymmetric hydroamination reaction between aniline and di(phenylethynyl)phenylphosphine.⁸³

The analogous asymmetric hydrophosphination is relatively new but has rapidly become a potentially effective synthetic strategy for the preparation of chiral phosphines which are useful as ligands in asymmetric synthesis and biological studies. Similar to the hydroamination reaction, two types of reaction mechanism have been reported for metal ion induced hydrophosphination reaction: Glueck and his co-workers observed the oxidative addition of a secondary phosphine followed by olefin insertion¹⁰⁰ while Togni's group observed the coordination of the olefin followed by addition of a secondary phosphine across the C-C double bond.¹⁰¹ On the other hand, it has been shown that the asymmetric hydrophosphination of vinylic phosphines involves the simultaneous coordination of both the reacting vinylic phosphine and the secondary phosphine on the chiral metal complex.^{92, 94, 95, 102} We recently reported the synthesis of (-)-prophos **151** with high enantioselectivity via an asymmetric hydrophosphination reaction⁹⁵.

(-)-prophos

151

Today, asymmetric hydroamination can be employed for the routine synthesis of chiral amine compounds¹⁰³ while the corresponding hydrophosphination reaction provides an alternative way of preparing chiral organophosphorus compounds^{92, 94, 95, 100-102}. On the other hand, the number of reports on the addition of As-H moiety to C=C or C≡C bonds is few⁵⁴. Certainly no asymmetric syntheses involving As-H bond activation have been reported hitherto. Such a process should generate potentially powerful and stereospecific

arsenic chelating agents for synthetically important second-row and third-row transition metals. In this work, the synthesis of optically active P-As hetero-bidentate ligands via the first asymmetric hydroarsination reaction is reported.

4.2 Results and Discussion

The asymmetric synthesis of new chiral bidentate ligands such as prophos⁹⁵ **151**, functionalized chiral diphosphines^{83, 92, 94} and hetero-bidentate ligands (*e.g.* P-N)⁸³ benefited from the stereochemical control by the chiral auxiliary ortho-metalated dimethyl[1-(1-naphthyl)ethyl]amine. In contrast with its phenylene counterpart, the five-membered organometallic ring formed in a square-planar palladium complex adopts a stable conformation, *i.e.*: λ helicity for *S* absolute configuration on the stereogenic carbon and δ helicity for the *R* absolute configuration. This unique stereochemical feature of the chiral naphthylamine ring is due to the internal steric repulsion between the methyl substituent on the stereogenic carbon and its neighboring naphthylamine proton. Hence, in the asymmetric synthesis of chiral bidentate ligands, the number of chiral centers newly formed with the bidentate ligand independently dictates the number of diastereomers that will be formed.

4.2.1 Hydroarsination of Diphenylvinylphosphine

In the absence of a metal ion, no reaction was observed between diphenylarsine and diphenylvinylphosphine. Thus, the monodentate phosphine was coordinated to the dimeric chiral template (*S_C*)-**58** via a regiospecific bridge-splitting process¹⁰⁴ (Scheme 4.2). It is important to note that the chloro ligand in the template complex (*S_C*)-**152** and in similar complexes is well known to be kinetically and thermodynamically stable and is not readily displaced by other strong ligands such as monodentate phosphines^{92, 94, 95, 102} and amines⁸³. In order to provide a coordinate site for the reacting diphenylarsine,

(*S_C*)-**152** was treated with a silver salt prior to the introduction of the secondary arsine into the reaction mixture.

Scheme 4.2. Synthetic route for the preparation of (*S_C*)-**154a** and (*S_C*,*S_P*/*R_P*)-**154b**

The hydroarsination reaction between diphenylvinylphosphine and diphenylarsine was monitored by ^{31}P NMR spectroscopy. The addition reaction was found to proceed in a facile manner in methanol at 65°C and was complete within 24 hours.

It was observed that upon addition of the secondary arsine at room temperature the solution changed from light yellow to light orange and upon heating the product precipitated out of solution as a white solid. The crude product was purified via silica gel chromatography using ethyl acetate-hexane and dichloromethane-hexane mixtures as eluents. (*S_C*)-**154a** was obtained as colorless rectangular crystals from a mixture of dichloromethane and diethyl ether in 37% yield; $[\alpha]_D^{25} +55.4$ (*c* 0.19, CH₂Cl₂).

4.2.1.1 Single Crystal X-ray Crystallography

The molecular structure of (*S_C*)-**154a** is depicted in Figure 4.1. Selected bond lengths and angles are shown in Table 4.1. The asymmetric skew conformation of λ helicity of the organometallic ring of (*S_C*)-**58** was retained in the complex, wherein the Me group on the stereogenic carbon occupies the axial site. The newly formed As-P bidentate ring adopts the asymmetric skew conformation with λ helicity. The inter-chelate steric repulsion between the AsPh₂ and the NMe₂ groups is clearly reflected by the larger N(1)-Pd(1)-As(1) angle [99.9(1)°] compared with the C(1)-Pd(1)-P(1) angle [94.8(1)°]. The bond distance Pd(1)-As(1) [2.44(0) Å] is significantly longer than the bond distance Pd(1)-P(1) [2.25(1) Å]. The C(15)-C(16) [1.52(0) Å] bond of the carbon backbone indicates a single bond.

Figure 4.1. Molecular structure and absolute configuration of (*S*_C)-154a

Table 4.1. Selected bond lengths (Å) and angles (°) for complex (S_C)-154a

Pd1-C1	2.043(2)	C1-Pd1-N1	80.8(1)
Pd1-N1	2.128(2)	C1-Pd1-P1	94.8(1)
Pd1-P1	2.246(1)	N1-Pd1-P1	174.6(1)
Pd1-As1	2.441(1)	C1-Pd1-As1	178.6(1)
As1-C23	1.928(3)	N1-Pd1-As1	99.9(1)
As1-C17	1.929(2)	P1-Pd1-As1	84.3(1)
As1-C16	1.966(3)	C15-P1-Pd1	110.2(1)
P1-C35	1.804(2)	C16-As1-Pd1	105.4(1)
P1-C29	1.817(2)	C17-As1-C16	103.4(1)
P1-C15	1.847(2)	C15-C16-As1	107.6(2)
C15-C16	1.525(3)	C16-C15-P1	109.8(2)

4.2.1.2 Two-dimensional ¹H-¹H ROESY NMR Spectroscopy Analysis of (S_C)-154a

The 2-dimensional ¹H-¹H ROESY NMR spectrum of (S_C)-**154a** in CD₂Cl₂ is depicted in Figure 4.2 with the numbering scheme in Figure 4.3. It is well-known that the 5-membered organometallic ring of an organopalladium complex consisting of the ortho-metalated dimethyl[(S)-1-(1-naphthyl)ethyl]amine auxiliary adopts the stable λ conformation in solution while the analogous *R* chiral auxiliary adopts the corresponding stable δ conformation. The characteristic NOE patterns observed for the ortho-metalated *S* naphthylamine ring consist of a set of signals: NOE signals (A-C) are observed due to the expected proximities of H(11) and the three methyl groups

from nitrogen and C(11), the stronger signal (F), is an indication of the closer proximity of the H(11) and H(8) of the naphthyl ring while the weaker signal (L) shows that the methyl group on the stereogenic carbon Me(12) exclusively adopts the axial position confirming the existence of a stable λ conformation. There is no signal showing any interaction between this methyl group and the axially oriented Me(13) on nitrogen, only its interaction with the equatorial methyl group Me(14) of nitrogen was observed. The presence of signals showing the interactions of Me(12) with both methyl groups on nitrogen will otherwise be observed when the ring adopts the stable δ conformation, that is when Me(12) is in equatorial position.

Usually, 5-membered bidentate rings composing of two donor atoms without any substituent within its backbone is well-known to undergo an equilibrium exchange between the δ and λ conformations in solution¹⁰⁵. In the case of complex (*S_C*)-**154a**, however, the newly formed 5-membered bidentate ring seems to adopt a stable λ conformation in solution as evident from its 2D ^1H - ^1H ROESY NMR Spectrum (Figure 4.2).

It can be observed that signal D shows a very strong interaction between the two equatorially oriented protons within the carbon backbone that point towards one another (Figure 4.3) when the 5-membered bidentate ring is in the λ conformation. The proton on C(15) that is equatorially disposed shows a sole interaction with the ortho-protons on the axial phenyl group of phosphorus (M). This result suggests that the 5-membered bidentate ring is locked in the λ conformation. Unexpectedly, the proton on C(16) shows a fairly strong interaction with H(8) although these two protons are relatively far from each other (J).

Figure 4.2. 2D-ROESY NMR spectrum of (*S_C*)-154a. Selected NOE Interactions: A: H₁₁-Me₁₂, B: H₁₁-Me₁₃, C: H₁₁-Me₁₄, D: H'₁₅-H'₁₆, E: Me₁₂-Me₁₄, F: H₁₁-H₈, G: Me₁₄-*o*-Ph_{As}, H: Me₁₃-*o*-Ph_{As}, I: Me₁₄-H₈, J: H'₁₆-H₈, K: undetermined, L: Me₁₂-H₈, M: H'₁₅-*o*-Ph_P, N: H₂-*o*-Ph_P

Figure 4.3. Numbering scheme and Dreiding diagram of (*S_C*)-154a

Regarding the possibility of equilibrium between the two conformations, the results of the 2D-ROESY NMR study may not be sufficient to confirm unambiguously the occurrence or non-occurrence of the equilibrium between the two conformations. In addition, the ^1H NMR spectrum of (*S_C*)-154a shows a disproportional integration of protons on the carbon backbone compared to that of its methyl analogue (*S_C*,*R_C*)-167 (see Section 4.2.5) (Figure 4.4b), which clearly showed each individual proton with expected integration intensity (Figure 4.4b). While it had already been shown from the 2D-ROESY that the 5-membered ring was locked in λ conformation in solution, any possibility of a dynamic equilibrium between λ and δ may still exist which may not be detectable at room temperature NMR spectroscopy.

Since, the ^1H NMR spectrum of (*S_C*)-154a in CDCl_3 did not exhibit peaks that were well resolved, the solvent was changed to CD_3CN . In this solvent it was observed from its spectrum (Figure 4.4a) that the integration of the protons within the carbon backbone is not proportional with the rest of the structure in contrast to the ^1H NMR of the methyl substituted analogue of this complex (Figure 4.4b), where integrations of the protons on the backbone are all proportional.

(a) ¹H NMR of (S_C)-154a in CD₃CN

(b) ^1H NMR of (S_C, R_C) -165 in CDCl_3

Figure 4.4.

The same disproportional integration was observed from the ^1H NMR spectrum of diphos ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) compared to its methyl substituted analogue, prophos⁹⁵ **151** when these two ligands were complexed with the chiral organo-palladium template (Figure 4.5).

Figure 4.5. Palladium(II) complexes of prophos 155 and diphos 156

Table 4.2. Selected ^1H NMR δ and integration of the carbon backbone protons of palladium(II) complexes of prophos 151 and diphos

	$\text{P}^1\text{HH}'$	$\text{P}^1\text{CHH}'$	P^2HMe	$\text{P}^2\text{HH}'$
(S_C, S_C) -155 (CDCl_3)	2.12-2.23 (1H)	2.55-2.64 (1H)	2.77-2.93 (1H)	-
(S_C) -156 (CD_3CN)	2.00-2.08 (1H)	2.09-2.13 (1H)	2.64-2.77 (1H)	2.78-2.87 (0.5H)

4.2.2 Asymmetric Hydroarsination of Divinylphenylphosphine

The reaction between divinylphenylphosphine and diphenylarsine was carried out following the same synthetic route as the previous reaction leading to (S_C) -154a (Scheme 4.2). Within 24 hours two diastereomers, at almost equal ratio, were identified by ^{31}P NMR spectroscopy. Stirring the reaction mixture for a further 2 more days resulted in a change in the diastereoselectivity ratio to 2:1 corresponding to (S_C, R_P) -154b and (S_C, S_P) -154b with ^{31}P NMR chemical shift of 56.0 (s) and 59.1 (s), respectively. Attempts to separate the diastereomers by silica gel chromatography proved to be futile. However, fractional crystallization from dichloromethane-diethyl

ether solvent system produced colorless needle-like crystals of (*S_C*,*S_P*)-**154b** in 17% isolated yield, $[\alpha]_{\text{D}} +38.2$ (*c* 0.1, CH₂Cl₂).

The more soluble major isomer could not be crystallized even after trying various solvent systems. Hence, the semi-pure solution of the major isomer was reacted with concentrated HCl solution to give the di-chloro complex (*R_P*)-**158** as a yellow solid with ³¹P NMR δ 63.9 (s) and a ¹H NMR spectrum, which shows broad signals of the protons. The solution of the di-chloro complex was treated with aqueous solution of KCN to liberate the bidentate ligand (*S_P*)-**159**; ³¹P NMR δ -16.1 (s), 84% yield, $[\alpha]_{\text{D}} -17.8$ (*c* 0.16, CH₂Cl₂). The free ligand was found to be moderately sensitive in air. This ligand was then re-coordinated with the *R* handform of the dimeric complex (*R_C*)-**58** to give the epimer (*R_C*,*R_P*)-**155** (Scheme 4.3). This chiral complex was easily crystallized from dichloromethane-diethyl ether solvent system as colorless needle-like prisms in 89% isolated yield, $[\alpha]_{\text{D}} -38.5$ (*c* 0.1, CH₂Cl₂).

Scheme 4.3. Reaction route in obtaining the less soluble epimer $(R_C, R_P)\text{-154}$

4.2.2.1 Single Crystal X-ray Diffraction analysis

The molecular structure and absolute configuration of $(S_C, S_P)\text{-154b}$ have been confirmed by X-ray crystallography (Figure 4.6). Selected bond lengths and angles are shown in Table 4.3. The 5-membered organometallic ring of this isomer has asymmetric skew conformation of λ helicity with the methyl substituent on the asymmetric carbon having an *S* absolute configuration occupying the axial site below the square plane. The asymmetric skew conformation of λ helicity was observed in the

newly formed As-P bidentate ring of (S_C, S_P)-**154b** wherein the phenyl group on the stereogenic phosphorus is equatorially located below the square plane. The phenyl groups on arsenic are in a pseudo-staggered orientation relative to the neighboring methyl groups on nitrogen. This arrangement gives a minimum inter-chelate steric repulsion that is present in the complex.

The molecular structure and absolute stereochemistry of the less soluble epimer (R_C, R_P)-**154** are shown in Figure 4.7. Selected bond lengths and angles are shown in Table 4.3. The 5-membered organometallic ring of (R_C, R_P)-**154** has asymmetric skew conformation of δ helicity with the methyl substituent on the asymmetric carbon having an *R* absolute configuration occupying the axial site above the square plane. The As-P bidentate ring has an asymmetric skew conformation of δ helicity with the phenyl group on chiral phosphorus equatorially oriented above the coordination plane. The phenyl groups on arsenic are in pseudo-staggered orientation with the methyl groups on nitrogen showing this conformation has the minimum inter-chelate steric repulsion.

Figure 4.6. Molecular structure and absolute configuration of (S_C, S_P)-154b

Figure 4.7. Molecular structure and absolute configuration of (*R_C*,*R_P*)-154

Table 4.3. Selected bond lengths (Å) and angles (°) for complex (S_C,S_P)-154b and (R_C,R_P)-154

	Molecule (S_C,S_P)-154b	Molecule (R_C,R_P)-154
Pd1-C1	2.050(4)	2.065(5)
Pd1-N1	2.122(4)	2.118(4)
Pd1-P1	2.242(4)	2.249(1)
Pd1-As1	2.439(1)	2.447(1)
As1-C21	1.929(4)	1.938(5)
As1-C15	1.933(4)	1.939(6)
As1-C27	1.956(4)	1.959(5)
P1-C28	1.842(5)	1.850(6)
P1-C29	1.793(5)	1.790(7)
P1-C31	1.812(4)	1.813(6)
C27-C28	1.534(7)	1.535(8)
C29-C30	1.301(9)	1.317(10)
C1-Pd1-N1	80.9(1)	81.2(2)
C1-Pd1-P1	97.2(1)	96.9(1)
N1-Pd1-P1	174.3(2)	174.6(1)
C1-Pd1-As1	178.3(2)	178.7(2)

N1-Pd1-As1	97.8(1)	97.7(1)
P1-Pd1-As1	83.9(1)	84.1(1)
C27-As1-Pd1	105.2(1)	105.1(2)
C29-P1-Pd1	111.3(2)	111.4(2)
C28-C27-As1	106.0(3)	105.9(3)
C27-C28-P1	109.3(3)	109.6(4)
C30-C29-P1	123.9(5)	123.8(6)

4.2.2.2 NMR Spectroscopy Analysis of (*S_C*,*R_P*)-**154b** and (*S_C*,*S_P*)-**154b**

The ^1H NMR spectrum of (*S_C*,*R_P*)-**154b** in CDCl_3 shows that the resonance of the proton *alpha* to the metalated carbon (H_γ) (Figure 4.8) of the naphthalene ring is noticeably shifted to higher field while the protons of the phenyl group *ortho* to phosphorus had greatly shifted to the lower field. Similar chemical shifts have been observed for analogous complexes bearing a chiral phosphorus or arsenic donor atom *cis* to the naphthalenic carbon^{39, 50}. These complexes demonstrated the strong shielding effect of the phenyl group on arsenic or phosphorus on the neighboring proton on the naphthyl group.

(S_C,R_P)-154b

Figure 4.8. The shielding effect of phenyl on phosphorus on $\text{H}\gamma$

4.2.3 Hydroarsination Reactions in Diphenyl-1-propynylphosphine and Di-1-propynylphenylphosphine

The addition of diphenylarsine to an electron rich alkynylphosphine was also investigated. In contrast to the previous reactions, this hydroarsination reaction of diphenylarsine with diphenyl-1-propynylphosphine proceeded in dichloromethane. Electronically, the β -carbon of the alkyne moiety is more deficient than the alkene, hence the addition of As-H across the multiple bonds is possible even in a slightly polar solvent such as dichloromethane.

The addition of diphenylarsine to (*S_C*)-**160a** (R₁=propynyl, R₂=phenyl) proceeded in a facile manner at room temperature and was complete within 24 hours (Scheme 4.4). The ³¹P NMR of the product in CDCl₃ shows a peak at δ 52.3. This complex was unable to be isolated by crystallization.

Scheme 4.4. Hydroarsination of diphenyl-1-propynylphosphine

The solution of $(S_C)\text{-161}$ was therefore treated with concentrated solution of HCl to remove the chiral auxiliary forming a di-chloro complex of the product, **162**

(Scheme 4.4). This di-chloro complex was obtained as yellow micro-crystals from dichloromethane-diethyl ether mixture. The ^{31}P NMR shows a resonance at δ 63.7 (s) in CDCl_3 .

The reaction between (*S_C*)-**160b** ($\text{R}_1=\text{R}_2=\text{propynyl}$) and diphenylarsine under the same condition as above did not give any hydroarsination product. Decomposition occurs instead. The same failure is met when the reaction was conducted in methanol (Scheme 4.5).

Scheme 4.5. Asymmetric hydroarsination of di-1-propynylphenylphosphine

4.2.3.1 X-ray Crystallographic Analysis

The molecular structure of complex **162** was studied by X-ray crystallography and showed that the 5-membered bidentate ring is in a regular square planar configuration adopting an envelope conformation. The molecular structure is shown in Figure 4.9 while selected bond lengths and angles are shown in Table 4.4. The angles As(1)-C(14)-C(13) [121.0(2)°] and P(1)-C(15)-C(14) [122.1(1)°] are within the range of an alkene moiety. In addition, the bond length [1.34(0) Å] of C(14)-C(15) and the angles [114.0(2)-124.8(2)°] around the sp² carbons are consistent with a C-C double bond.

Figure 4.9. Molecular structure of 162

Table 4.4. Selected bond lengths (Å) and angles (°) for complex 162

Pd1-P1	2.234(1)	P1-Pd1-As1	85.8(1)
Pd1-As1	2.314(1)	P1-Pd1-Cl2	93.2(1)
As1-C1	1.914(2)	As1-Pd1-Cl2	178.6(2)
As1-C7	1.921(2)	P1-Pd1-Cl1	88.1(2)
As1-C14	1.937(2)	Cl2-Pd1-Cl1	92.9(1)
P1-C15	1.798(2)	C14-As1-Pd1	107.4(1)
P1-C22	1.815(2)	C15-P1-Pd1	110.6(1)
P1-C16	1.832(2)	C15-C14-As1	114.0(2)
C13-C14	1.488(3)	C13-C14-As1	121.0(2)
C14-C15	1.343(3)	C14-C15-P1	122.1(2)
		C15-C14-C13	124.8(2)

4.2.4 Asymmetric Hydroarsination of Diphenyl-1-propenyl-(*E*)-phosphine

In the absence of a metal ion, no reaction was observed between diphenylarsine and the vinylphosphine. Thus, the monodentate (*E*)-propenyldiphenylphosphine was coordinated to the dimeric chiral template (*S_C*)-**58** via a regiospecific bridge-splitting process (Scheme 4.6).¹⁰⁴ The asymmetric hydroarsination reaction was monitored by ³¹P NMR spectroscopy and was found to proceed in a facile manner at room temperature in methanol and completed within 24 hours. Two diastereomeric complexes (*S_C*,*R_C*)-**165** and (*S_C*,*S_C*)-**165** were generated with a diastereoselectivity of 8:1, respectively. While it has been observed that the addition of the secondary phosphine (Ph₂PH) resulted in *cis-trans* regioisomers of the products⁹⁵, the addition of diphenylarsine is regiospecific wherein the

phosphorus atom occupies the coordination site *trans* to nitrogen exclusively. The high regioselectivity observed in the present case was in agreement with those observed for similar arsenic-phosphorus heterobidentate ligands³⁹. No other products were detected by the 202 MHz ³¹P NMR spectroscopy. The two diastereomeric products could be separated into their stereoisomerically pure forms by fractional re-crystallization from dichloromethane-diethyl ether. The less soluble major isomer, (*S*_C,*R*_C)-**165** was isolated as colorless square plates in 34% yield, [α]_D +56.8 (*c* 0.2, CH₂Cl₂). The ³¹P NMR spectrum of (*S*_C,*R*_C)-**165** in CDCl₃ exhibited a singlet at δ 51.4. The crystallization of the more soluble minor isomer (*S*_C,*S*_C)-**165** was less effective and it was isolated only in 6% yield as colorless microprisms with [α]_D +64.0 (*c* 0.1, CH₂Cl₂). The ³¹P NMR spectrum of this minor product in CDCl₃ exhibited a singlet at δ 51.2.

Scheme 4.6. Synthetic route for the preparation of $(S_C,R_C/S_C)\text{-}165$

4.2.4.1 Single Crystal X-ray Diffraction Analysis

The molecular structure and the absolute stereochemistry of the major product $(S_C,R_C)\text{-}165$ were determined by single crystal X-ray diffraction analysis. There are two crystallographically distinguished molecules in the asymmetric unit with slightly different bond lengths and angles. For simplicity, Figure 4.10 shows only the ORTEP drawing of molecule 1. Selected bond lengths and angles are listed in Table 4.5. The coordination geometry about palladium correlates with data on all previous complexes containing the ortho-metalated dimethyl[1-(α -naphthyl)ethyl]amine ring.⁹⁵ The 5-membered organometallic ring containing the palladium atom has asymmetric skew

conformation of λ helicity with the methyl substituent on the asymmetric carbon stereogenic center of *S* absolute configuration occupying the axial site. The P and As donor atoms of the new hetero-bidentate are bonded regiospecifically to the palladium atom, with the softer phosphorus donor taking up the position *trans* to the NMe₂ group. In contrast to the organometallic ring, the new As-P bidentate chelate adopts the asymmetric skew conformation of λ helicity with the methyl substituent on the asymmetric C(28) stereocenter of *R* absolute configuration occupying the sterically favorable equatorial position. All the substituents at C(28) and the bulky As-Ph groups adopt a staggered orientation. The inter-chelate steric repulsion between the NMe₂ and the AsPh₂ groups is reflected clearly by the larger N(1)-Pd(1)-As(1) angle [99.5(2)°] as compared with the smaller C(1)-Pd(1)-P(1) angle [97.0(1)°]. The Pd(1)-As(1) bond distance [2.48(1) Å] is significantly longer than the Pd(1)-P(1) bond [2.25(1) Å]. The C(28)-C(29) bond distance [1.54(1) Å] is consistent with a typical C-C single bond, while the angles around C(28) are consistent with that at tetrahedral carbon.

Figure 4.10. Molecular structure and absolute configuration of the cationic complex (S_C,R_C)-1

Table 4.5. Selected bond lengths (Å) and angles (°) for complex (S_C,R_C)-165 and (S_C,S_C)-165

	Molecule (S _C ,R _C)-165	Molecule (S _C ,S _C)-165
Pd1-C1	2.051(5)	2.051(3)
Pd1-N1	2.144(5)	2.138(2)
Pd1-P1	2.255(2)	2.266(1)
Pd1-As1	2.484(1)	2.418(1)
As1-C21	1.936(3)	1.920(3)
As1-C15	1.948(6)	1.915(4)
As1-C28	1.983(6)	1.966(3)
P1-C30	1.809(5)	1.818(3)
P1-C36	1.821(6)	1.820(3)
P1-C29	1.824(5)	1.843(3)
C27-C28	1.511(8)	1.486(5)
C28-C29	1.541(8)	1.518(5)
C1-Pd1-N1	80.4(2)	81.4(1)
C1-Pd1-P1	97.0(1)	97.6(1)
N1-Pd1-P1	177.3(2)	175.9(1)
C1-Pd1-As1	177.2(2)	172.7(1)
N1-Pd1-As1	99.5(2)	96.8(1)
P1-Pd1-As1	83.1(1)	84.6(1)
C29-P1-Pd1	109.2(2)	110.3(1)
C28-As1-Pd1	107.1(1)	104.1(1)
C27-C28-C29	112.0(5)	114.9(3)

C27-C28-As1	116.6(5)	115.0(3)
C29-C28-As1	106.4(4)	104.4(2)
C28-C29-P1	114.0(4)	112.2(2)

The molecular structure and absolute configuration of the minor isomer (*S_CS_C*)-**165** were determined by single crystal X-ray diffraction analysis. Figure 4.11 depicts the ORTEP drawing of the molecule. Selected bond lengths and angles are shown in Table 4.5. The absolute configuration and conformation of the 5-membered organometallic ring were similar to the previous major diastereomer. The As-P bidentate chelate was similarly arranged regioselectively within the coordination plane wherein the phosphorus donor atom was located in the position *trans* to nitrogen. In contrast to the major diastereomeric complex, the As-P bidentate chelate adopts the asymmetric skew conformation of δ helicity with the methyl substituent on the stereogenic C(28) of *S* absolute configuration occupying the sterically favorable equatorial position. However, the same staggered orientation was observed between the substituents on C(28) and of the arsenic atom. The repulsive strain between NMe₂ and AsPh₂ groups of this complex is smaller than the major diastereomer based on the N(1)-Pd(1)-As(1) angle [96.8(1)° versus 99.5(2)°]. The Pd(1)-As(1) bond distance [2.42(0)Å] is longer than the Pd(1)-P(1) bond [2.27(1)Å]. The C(28)-C(29) bond [1.51(1)Å], which is consistent with a C-C single bond, is shorter than that of the previous diastereomer. The geometry around C(28) is consistent with tetrahedral carbon.

Figure 4.11. Molecular structure and absolute configuration of the cationic complex (S_C, S_C)-165

4.2.4.2 Mechanistic study

It is noteworthy that the current asymmetric hydroarsination reaction could only be induced effectively in polar solvents, such as methanol. The reaction failed when non-alcoholic or non-polar solvents, such as dichloromethane and benzene, were employed. From a mechanistic standpoint, the simultaneous coordination of the diphenylarsine and the methyl-substituted vinylphosphine on the chiral palladium template polarizes the As-H and the vinylic C=C bond concurrently. An intermediate involving the deprotonated form of the highly reactive coordinated arsenido ligand could be generated. This highly reactive nucleophile can be stabilized by the polar solvent, which promotes the nucleophilic addition reaction to form the new As-C bond. Furthermore, an alcoholic solvent would facilitate in the subsequent protonolysis process in this metal complex promoted hydroarsination reaction. Indeed the protonolysis of the P-C carbon may be initiated by the proton of the methanol solvent, which may be regenerated subsequently by proton transfer from the As-H moiety. A similar stepwise proton transfer process involving coordinated secondary phosphine has been described previously.¹⁰⁶ Meek *et. al.* observed that the reaction between $\text{PtCl}_2(\text{cyppH})$ **168** ($\text{cyppH} = \text{Cy}_2\text{P}(\text{CH}_2)_3\text{PPh}$) with diphenylvinylphosphine **169** in ethanol without any catalyst such as Et_3N or $\text{KO}t\text{-Bu}$ occurs but in a much slower rate than when Et_3N is present.¹⁰⁶ It appears that ethanol stabilizes the phosphido nucleophile that was formed, which then attacks the vinyl group and may have subsequently undergone a proton exchange (Scheme 4.8).

Scheme 4.7. Hydrophosphination of the vinylphosphine by the platinum(II) complex of secondary phosphine

4.2.4.3 Stereochemical Study of the Bidentate Complexes (S_C, R_C)-165 and (S_C, S_C)-165

The asymmetric formation of the bidentate As-P within the palladium template may proceed via two possible pathways (Figure 4.12). The most likely pathway wherein the reaction went through to form the major product is Pathway A. This is due to the reduced steric hindrances between the inter-chelate Me and Ph groups on the nitrogen and arsenic donor atoms, respectively. Apparently, this steric effect between the neighboring donor groups is not large enough to totally remove the possibility of Pathway B in which only around 10% of the products had resulted.

Figure 4.12. Pathways for the stereoselective formation of the products of asymmetric hydroarsination of 1-propenyl-(*E*)-diphenylphosphine

4.2.4.4 Liberation of (+)-1-diphenylphosphino-2-diphenylarsino propane, (*R_C*)-169

The new As-P chiral bidentate ligand generated in the hydroarsination reaction could be liberated efficiently from the chiral metal template (Scheme 4.8). Treatment of the palladium template (*S_C*,*R_C*)-165 with aqueous potassium cyanide gave the optically pure (+)-1-diphenylphosphino-2-diphenylarsino propane (*R_C*)-169 as a moderately air-sensitive colorless oil in 90% yield, $[\alpha]_D +131.0$ (*c* 0.2, CH₂Cl₂). The ³¹P NMR spectrum of (*R_C*)-169 in CDCl₃ exhibited a singlet at δ -20.5. The optical purity of the chiral As-P bidentate ligand was confirmed by the re-preparation of (*S_C*,*R_C*)-165 from the liberated (*R_C*)-169 and the palladium(II) dimer (*S_C*)-58 (Scheme

4.8). The ^{31}P NMR spectroscopy of the crude product indicated the presence of a single product [δ 51.4].

Scheme 4.8. Liberation of (+)-1-diphenylphosphino-2-diphenylarsinopropane, (R_C) -169

4.2.5 Asymmetric Hydroarsination of Di-1-propenyl-(*E*)-phenylphosphine

Similar to the previous reactions the reaction between the diphenylarsine and the di-1-propenyl-(*E*)-phenylphosphine did not occur without the presence of a metal ion. Therefore, the monodentate vinyl phosphine was coordinated to the dimeric chiral template (S_C) -58 via a regiospecific bridge-splitting process (Scheme 4.9). In order to provide a coordination site for the reacting diphenylarsine, (S_C) -170 was treated with silver perchlorate prior to the introduction of the secondary arsine into the reaction mixture.

The asymmetric hydroarsination reaction proceeded in a facile manner in methanol at room temperature and completed within *ca.* 24 hours as shown by its ^{31}P

NMR spectrum. Four diastereomerically distinct complexes were formed with a stereoselectivity of 1:16:2:15 (Figure 4.13, Table 4.6). These four diastereomeric products were the result of the two newly created chirality centers (stereogenic C and P) on the carbon backbone and the phosphorus donor atom, respectively. As what was initially observed from the previous bidentate complexes synthesized and from other arsenic-phosphorus bidentate ligands³⁹, the two donor atoms in these complexes do not exhibit any *cis-trans* regioisomerism, that is, the phosphorus atom occupies the site *trans* to nitrogen at all times in solution. This will be showed later through the crystal X-ray diffraction and 2D ROESY NMR studies of the diastereomeric products.

Scheme 4.9. Synthetic route for the asymmetric hydroarsination of di-1-propenyl-(*E*)-phenylphosphine with diphenylarsine

Figure 4.13. ^{31}P NMR spectrum of the asymmetric hydroarsination between diphenylarsine and di-1-propenyl-(*E*)-phenylphosphine

Table 4.6. ^{31}P and ^1H NMR Spectroscopy chemical shifts of selected protons of the diastereomers

		^{31}P NMR δ	NMe _{ax}	NMe _{eq}	H(2)	H(3)	<i>o</i> -Ph
A	(<i>S_C,R_C,S_P</i>)- 172	47.93(s)	2.61(s)	2.88(d)	7.06(dd)	7.20(d)	
B	(<i>S_C,R_C,R_P</i>)- 172	45.45(s)	2.64(s)	2.89(d)	6.94(dd)	7.27(d)	8.13(dd)
C	(<i>S_C,S_C,S_P</i>)- 172	49.10(s)	2.94(s)	2.70(d)			
D	(<i>S_C,S_C,R_P</i>)- 172	46.83(s)	2.96(s)	2.66(d)	6.81(dd)	7.20(d)	7.97(ddd)

The diastereomers could not be successfully separated using silica gel chromatography. However they could be separated into their stereochemically pure

forms by fractional re-crystallization. The crystals of diastereomer (S_C, R_C, S_P)-**172** (corresponding to peak A in Figure 4.13) was obtained from a solution of dichloromethane and diethyl ether as colorless square-plate crystals in 23% yield $[\alpha]_D +8.7$ (c 0.1, CH_2Cl_2). The ^{31}P NMR spectrum of this diastereomer in CDCl_3 exhibited a singlet at δ 47.9. The crystals of the diastereomer (S_C, S_C, R_P)-**172** (corresponding to peak D in Figure 4.13) was obtained from the same solvent mixture as yellow rectangular prisms in 2.9% yield $[\alpha]_D +71.0$ (c 0.3, CH_2Cl_2). The ^{31}P NMR spectrum of this diastereomer in CDCl_3 exhibited a singlet at δ 46.8. The more soluble diastereomers (S_C, R_C, R_P)-**172** and (S_C, S_C, S_P)-**172** (corresponding to peaks B and C in Figure 4.13) remained in solution during the whole re-crystallization process and further purification using silica gel chromatography was futile. The 2D-ROESY NMR of (S_C, R_C, R_P)-**172** was taken from this semi-pure solution to confirm its molecular structure and absolute stereochemistry. The isolation of (S_C, S_C, S_P)-**172** had faced the same failure using silica gel chromatography. The absolute configuration of this isomer was confirmed by comparison of its ^1H NMR spectrum with that of (S_C, S_C, R_P)-**172**.

4.2.5.1 Single Crystal X-ray Diffraction Analysis

a.) (S_C, R_C, S_P)-172 (Product A in Table 4.6)

The molecular structure and absolute stereochemistry of (S_C, R_C, S_P)-172 were determined by single crystal X-ray diffraction analysis. Figure 4.14 shows the ORTEP picture of the molecule. Selected bond lengths and angles are listed in Table 4.7. The 5-membered organometallic ring of the ortho-metalated dimethyl[1-(α -naphthyl)-ethyl]amine ring retained its asymmetric skew conformation of λ helicity with the methyl substituent on the asymmetric stereogenic carbon having an *S* absolute configuration occupying the axial site. Similar to previous complexes, the P and As donor atoms of the new hetero-bidentate ligand are bonded regiospecifically to the palladium atom, wherein the phosphorus is located in a *trans* position relative to nitrogen. The newly formed 5-membered bidentate ring, on the other hand, adopts the same λ conformation with the methyl group on the stereogenic carbon C(28) of *R* absolute configuration occupying the sterically favorable equatorial position and with the propenyl group on asymmetric phosphorus stereocenter of *S* absolute configuration occupying the sterically favorable axial position. The angle within N(1)-Pd(1)-As(1) [96.8(1)°] is surprisingly smaller compared with the same angle in the analogous (S_C, R_C)-165 [99.5(2)°] considering that they have the same configuration on C(28) and conformation of the bidentate ring (Figure 4.15). This angle is relatively smaller compared to C(1)-Pd(1)-P(1) angle [97.0(1)°] due to the steric repulsion between the proton on C(2) of the naphthyl group and the proton of the propenyl group on phosphorus. The Pd(1)-As(1) bond distance [2.44(1)Å] is notably longer than Pd(1)-P(1)

Figure 4.14. Molecular structure and absolute configuration of the cationic (S_C, R_C, S_P)-172 (Product A)

Table 4.7. Selected bond lengths (Å) and angles (°) for complex (S_C,R_C,S_P)-172 and (S_C,S_C,R_P)-172

	Molecule (S_C,R_C,S_P)-172	Molecule (S_C,S_C,R_P)-172
	Product A	Product D
Pd1-C1	2.062(5)	2.042(4)
Pd1-N1	2.131(3)	2.143(3)
Pd1-P1	2.259(2)	2.281(1)
Pd1-As1	2.445(1)	2.467(1)
As1-C15	1.940(5)	1.935(5)
As1-C21	1.949(5)	1.939(5)
As1-C27	-	1.983(5)
As1-C28	1.962(5)	-
P1-C29	1.844(6)	1.849(7)
P1-C30	1.790(6)	1.766(7)
P1-C33	1.806(5)	1.836(7)
C27-C28	1.503(8)	1.489(7)
C28-C29	1.513(9)	-
C30-C31	1.336(10)	1.156(10)
C27-C29	-	1.477(8)
C1-Pd1-N1	81.5(1)	80.2(2)
C1-Pd1-P1	97.0(1)	95.5(1)
N1-Pd1-P1	178.2(1)	173.8(1)
C1-Pd1-As1	177.1(1)	179.3(1)

N1-Pd1-As1	96.8(1)	100.4(1)
P1-Pd1-As1	84.6(1)	83.9(1)
C27-As1-Pd1	-	103.0(1)
C28-As1-Pd1	103.4(2)	-
C29-P1-Pd1	109.8(2)	110.3(2)
C27-C28-As1	115.8(4)	-
C28-C27-As1	-	104.7(4)
C27-C29-P1	-	113.4(4)
C28-C29-P1	112.5(4)	-

bond distance of [2.26(0)Å]. The C(28)-C(29) bond distance [1.51(1)Å] is consistent with a typical C-C single bond length and the angles around C(28) are all consistent with tetrahedral carbon.

(S_C, R_C, S_P) -172

(S_C, R_C) -165

$$\theta_1 < \theta_2$$

Figure 4.15. The comparison of angle N(1)-Pd(1)-As(1) of (S_C, R_C, S_P) -172 and (S_C, R_C) -165

b.) (S_C, S_C, R_P)-172 (Product D from Table 4.6)

The molecular structure and absolute stereochemistry of (S_C, S_C, R_P)-172 were determined by single crystal X-ray diffraction analysis. Figure 4.16 shows the ORTEP picture of the molecule. Selected bond lengths and angles are listed in Table 4.7. The conformation of the 5-membered organometallic ring, the absolute configuration of its stereogenic carbon and the regiochemistry around the square planar palladium are all the same as the previous diastereomeric complex. The newly formed 5-membered bidentate ring, on the other hand, adopts the δ conformation with the methyl group on the stereogenic carbon C(27) of S absolute configuration occupying the sterically favorable equatorial position and with the propenyl group on asymmetric phosphorus stereocenter of R absolute configuration occupying the sterically favorable axial position. The angle within N(1)-Pd(1)-As(1) [$100.4(1)^\circ$] is significantly larger than that of the previous complex. This is because when the newly formed bidentate ring is in δ conformation, the Me and Ph groups of arsenic and nitrogen respectively are in pseudo-eclipsed orientation hence, the interchelate repulsion between the two rings is greater. The C(1)-Pd(1)-P(1) angle [$95.5(1)^\circ$] is relatively smaller than the previous diastereomer because the steric effect between the phenyl group of phosphorus and that of the naphthyl group will be less than when the vinyl group is interacting with the naphthyl group. The Pd(1)-As(1) bond distance [$2.47(0)\text{\AA}$] is remarkably longer than Pd(1)-P(1) bond distance of [$2.28(0)\text{\AA}$]. The C(27)-C(29) bond distance [$1.48(1)\text{\AA}$] is consistent with a typical C-C single bond length and the angles around C(27) are all consistent of a tetrahedral carbon.

Figure 4.16. Molecular structure and absolute configuration of the cationic (S_C, S_C, R_P)-172 (Pr) D)

4.2.5.2 Two dimensional ^1H - ^1H ROESY NMR of (S_C, R_C, R_P) -**172**

The molecular structure and absolute configuration of the more soluble diastereomer (S_C, R_C, R_P) -**172** were determined from the 2D ^1H - ^1H ROESY NMR of this diastereomer taken from its semi-pure solution consisting of a small amount of the three other isomers as seen from its ^{31}P NMR spectrum.

Similar to the previous complex above, the 5-membered organometallic ring of the organopalladium complex consisting of the ortho-metalated dimethyl[(*S*)-1-(1-naphthyl)ethyl]amine is locked in λ conformation in solution when the stereogenic carbon of the chiral auxiliary has an *S* absolute configuration (signals A, B, C, G and W). This locking is confirmed through 2D ^1H - ^1H ROESY NMR spectroscopy as shown in Figure 4.17 by the absence of the NOE interaction between the axially oriented methyl group Me(12) on the stereogenic carbon and the axially oriented methyl group of nitrogen Me(13) in *trans* geometry with each other. The absolute configuration of the new stereogenic carbon of (S_C, R_C, R_P) -**172** and the conformation of the bidentate ring are believed to be similar with (S_C, R_C, S_P) -**172** based on the similarities in pattern of the relative positions of the ^1H chemical shifts of the methyl groups on nitrogen Me(13) and Me(14) and of the observed high-field shift of H(2) on the naphthyl ring of both diastereomers (Table 4.6). These claims were confirmed by analyzing the 2D ROESY NMR spectrum below. The signal (D) which shows the interaction between the axial proton on C(17) and Me(15) within the backbone is relatively stronger than (F) which is the interaction between this methyl group and the equatorial proton on the same C(17) carbon. This difference in signal intensity shows that the axial proton of C(17) and Me(15) are both below the square plane. Similarly, the signal (I) is clearly stronger than (J) since the interacting protons on the former

signal are both on the same side of the square plane. Therefore, C(16) has an *R* absolute configuration and the 5-membered bidentate ring adopts the stable λ conformation.

Figure 4.17. 2D-ROESY NMR of (S_C, R_C, R_P) -172. Selected NOE Interactions: A: H₁₁-Me¹³, H₁₁:Me¹³, C: H₁₁:Me¹⁴, D: PCHH'-Me¹⁵, E: AsCHMe-Me¹⁵, F: PCHH'-Me¹⁵, G: Me¹²-Me¹⁴, PCHH'-PCHH', I: PCHH'-AsCHMe, J: PCHH'-AsCHMe, K: Me¹⁴-Me¹³, L: H₁₈-H₁₉, M: H₁₈-H₁₉, N: H₂-O-PhP, O: H₃-H₄, P: undetermined, Q: H₁₉-Me²⁰, R: H₁₈-Me²⁰, S,T: Me¹²-H₈, M₁₂-O-Ph, U:AsCHMe-O-PhAs_{eq}, V: Me¹⁴-OPhAs_{eq}, W: H₁₁-H₈.

4.2.5.3 Stereochemistry of the More Soluble Diastereomers

The square-planar palladium(II) complexes containing the ortho-metalated dimethyl[1-(α -naphthyl)ethyl]amine ring are known to exist in a single helicity, that is, the λ conformation with the *S* absolute configuration of stereogenic carbon and δ conformation for an *R* absolute configuration. The newly formed 5-membered bidentate ring is regiospecific wherein the softer π -acid phosphorus is located *trans* to the nitrogen group. Therefore, the sources of diastereomerism of the products are: (a) the relative configurations of the stereogenic carbon and phosphorus atom, and (b) the helicity of the 5-membered bidentate ring. There will be 8 possible diastereomeric products as a result.

Out of these 8 possible diastereomeric complexes, only 4 diastereomers were detected by the ^{31}P NMR spectroscopy that is, those attributed by the relative configurations of the two newly created stereogenic centers (C and P).

As observed from the X-ray molecular structure of (*S_C*,*R_C*,*S_P*)-**172** that the newly formed 5-membered bidentate ring adopted the stable λ conformation wherein the methyl groups of nitrogen and phenyl groups of the arsenic atom were in a pseudo-staggered orientation resulting in less interchelate-repulsion between this ring and the organometallic ring. The methyl group on the stereogenic carbon of the bidentate backbone was oriented equatorially avoiding a severe 1,3-diaxial repulsion that it could have experienced with the axially oriented olefin group on phosphorus.

The diastereomer (*S_C*,*R_C*,*R_P*)-**172** as shown in Figure 4.18 has the same λ conformation which positioned the phenyl groups of arsenic in a pseudo-staggered manner with the methyl groups on nitrogen and the methyl group on the carbon

backbone was in equatorial position. In this complex, the phenyl group is oriented axially. These two diastereomers are the two major isomeric products.

The last two groups of diastereomers in the figure have their 5-membered bidentate ring on a δ configuration wherein the phenyl groups of arsenic are pseudo-eclipsed with the methyl groups of nitrogen giving it a large interchelate-repulsion. The methyl group on the stereogenic carbon backbone is also in equatorial position and the diastereomers have their chirality in phosphorus of opposite configuration with one another.

Figure 4.18. Dreiding models of the actual conformations alongside the less stable conformations of the four diastereomeric products

4.2.5.4 Rotation Around the Pd-P Bond

The two major diastereomers were formed in almost equal ratio and both have the opposite configuration on their phosphorus atom. This poor selectivity may be due to the free rotation around the Pd-P bond of a monodentate phosphine which contains one phenyl and two propenyl groups. There is a possibility that the tetrahedral phosphine is free to rotate around the Pd-P bond of its organometallic complex. In a recent study about cyclopalladated complexes containing phosphine ligands, it was found that the rotation around the Pd-P bond of monophosphines containing at least one benzylic group in cyclopalladated complex is restricted whereas with that of triphenylphosphine is practically free to rotate.¹⁰⁷ In this case we deduced that the dipropenylphenylphosphine readily rotates around its Pd-P bond giving rise to equal opportunity for each olefin to be hydroarsinated. Replacing the proton on the carbon adjacent to the metallated carbon of the palladium complex with a bulkier group such as isopropyl or isobutyl group could restrict the rotation of the Pd-P bond. Another way could be by replacing the phenyl group on phosphorus atom with a bulkier group such as benzyl.

4.2.5.5 NMR Spectroscopic Analysis

The ^1H NMR studies of the two major diastereomers showed that the chemical shifts of their methyl groups on nitrogen are on the same field that is, the axially oriented methyl group is more shielded than the equatorial one. In the case of the two minor isomers, the ^1H NMR showed that the peaks due to the methyl groups were reversed. The 5-membered organometallic ring is always locked in a single

conformation, so one of the possible reasons for these observations was whenever this newly-formed ring is in λ conformation the neighboring methyl and phenyl groups are in pseudo-staggered orientation as in the case of the two major isomers. On the other hand, whenever the ring assumes the δ conformation the neighboring groups are in pseudo-eclipsed orientation. These relative positions between the methyl and phenyl groups affect the chemical shifts of the methyl groups.

A large high-field shift was observed for the naphthalenic proton H(2) and H(3) with the corresponding low-field shift of the ortho protons on the phenyl group of phosphorus for the diastereomers (S_C, S_C, R_P)-**172** and (S_C, R_C, R_P)-**172** (Table 4.6). Both of these isomers have their phenyl group on phosphorus oriented above the coordination plane, which in these positions provide shielding to the naphthalenic proton when the 5-membered organometallic ring is in λ conformation. Similar chemical shifts were seen in complexes of the *R* naphthyl template and ($S_{As}/R_{As}, S_P$)-**173** (see below).³⁹

A slightly shielded H(2) was observed in (S_C, R_C, S_P)-**172** (Table 4.6) because even though the phenyl group is pointing below naphthylene it is in equatorial

orientation making it relatively nearer than when it is axially oriented as in the case of (*S_C,S_C,S_P*)-**172**.

Therefore, generally, whenever the flat naphthyl group and the neighboring phenyl group were on the same side of the coordination plane that is, the two groups were in its nearest positions with each other, the shielding effect on the naphthalenic protons, H(2) and H(3) occurs.

4.2.6 Asymmetric Hydroarsination of Di-1-propenyl-(*Z*)-phenylphosphine

The asymmetric hydroarsination reaction was also performed with the *cis* isomer of the tertiary phosphine and was conducted through the same reaction conditions and reagents as the *trans* isomer (Scheme 4.10). The reaction was left stirring for 3 days at room temperature at end of which the reaction was complete. The reaction mixture consisted of four diastereochemically distinct products (Figure 4.19, Table 4.8) as shown from its ³¹P NMR spectrum with a stereoselectivity ratio of 5:1:7:2 respectively.

Fractional crystallization was attempted to separate the diastereomers. After a series of crystallization loops the diastereomer (*S_C,S_C,R_P*)-**176** was eventually isolated as colorless rectangular prisms from a dichloromethane-diethyl ether solvent system, 0.04 g (3% yield) [α]_D +150 (*c* 0.14, CH₂Cl₂). The isolation of the rest of the diastereomeric products was unsuccessful. Most of the crystals obtained contain at least two other diastereomers in a single crystal as shown by its ³¹P and ¹H NMR spectra. The molecular structure and absolute configuration of these diastereomers were determined using 2D ¹H-¹H ROESY NMR spectroscopy of their semi-pure solution.

Scheme 4.10. Synthetic route for the asymmetric hydroarsination of di-1-propenyl-(*Z*)-phenylphosphine with diphenylarsine

Figure 4.19. ^{31}P NMR spectrum of the diastereomeric products of di-1-propenyl-(Z)-phenylphosphine and diphenylarsine

Table 4.8. ^{31}P and ^1H NMR spectroscopy chemical shifts of selected protons of the diastereomers

		^{31}P NMR δ	NMe_{ax}	NMe_{eq}	H(2)	H(3)	<i>o</i> -Ph
A	(S_C, S_C, S_P) -176	29.46(s)	2.96(s)	2.72(d)		7.35(d)	7.88(dd)
B	(S_C, S_C, R_P) -176	36.26(s)	3.03(s)	2.46(d)	6.99(dd)		8.19(dd)
C	(S_C, R_C, R_P) -176	22.34(s)	2.60(s)	2.92(d)			7.82(dd)
D	(S_C, R_C, S_P) -176	32.37(s)					

4.2.6.1 Two dimensional ^1H - ^1H ROESY NMR Spectroscopy of (S_C, S_C, S_P) -**176**

Figures 4.20 and 4.21 show the numbering scheme and ^1H - ^1H ROESY NMR spectrum of (S_C, S_C, S_P) -**176** in CDCl_3 . The diastereomers A and C (Table 4.8) cannot be isolated in their pure crystalline form even after several crystallization loops. Hence, in a solution of dichloromethane and diethyl ether, yellow rectangular prism containing both isomers were obtained. The molecular structure and absolute configuration of (S_C, S_C, S_P) -**176** was confirmed by 2D-ROESY NMR spectroscopy. The crystal that was used for the ROESY consists of two diastereomers in which majority of it is the isomer (S_C, S_C, S_P) -**176** while the other minor isomer present was (S_C, R_C, R_P) -**176**, determined by comparison with the ^1H NMR of the previous isomer.

Similar to the previous complexes consisting of the ortho-metalated dimethyl[1-(1-naphthyl)ethyl]amine, the organometallic ring of (S_C, S_C, S_P) -**176** is locked in λ conformation in solution when the stereogenic carbon of the chiral auxiliary has an *S* absolute configuration (signals A, B, C, H and U). This locking is confirmed by 2D ROESY NMR spectroscopy (Figure 4.21) by the absence of the NOESY interaction between the axially oriented methyl group Me(12) on the stereogenic carbon and the axially oriented methyl group of nitrogen Me(14) in *trans* geometry (Figure 4.20). To determine the absolute configuration and the ring conformation of the newly formed 5-membered bidentate ring we have to similarly analyze the signals from the ROESY of the complex. Three sets of ROESY signals were analyzed to identify the absolute configuration and conformation of the bidentate ring: (a) Signal F shows a strong interaction between $\text{H}_b(29)$ and $\text{H}(28)$ which is

consistent with the relative positions of these protons when the 5-membered ring is in λ conformation (Figure 4.20). On the other hand, signal G shows as a very weak interaction between $H_a(29)$ and $H(28)$, which is not surprising since H_a is in *trans* position with $H(29)$. These findings support the λ conformation of the bidentate ring excluding any possibility of the formation of δ conformation in solution. (b) Signal J tells us that there is a presence of a very weak interaction between the axially oriented $Me(27)$ group with H_b . No signal representing the interaction $Me(27)-H_a$ is present from the ROESY plot which confirms that these two are axially oriented in *trans* geometry from one another. (c) Signal X shows us the interaction between $H(30)$ of the alkenyl group with the naphthalenic proton $H(2)$, which is located *alpha* to the metalated carbon. The absence of the high-field shift of this proton shows the absence of its interaction with the ortho-proton on the phenyl group of phosphorus. The absolute configuration of (S_C, R_C, S_P) -**176** was deduced from the absolute configurations of the other three diastereomers.

Figure 4.20. Dreiding diagram and numbering scheme of (S_C, S_C, S_P) -**176**

Figure 4.21. 2D ^1H - ^1H ROESY NMR of (S_C,S_C,S_P) -176. Selected NOE interactions: A: Me₁₄-H₁₁, B: Me₁₃-H₁₁, C: Me₁₂-H₁₁, D: Me₁₃-Me₁₄, E: H_a-H_b, F: H_b-H, G: H_a-H, H: Me₁₂-Me₁₃, I: H-Me₂₇, J: H_b-Me₂₇, K: H₃₁-H₃₂, L: Me₂₇-*o*-Ph_{As(eq)}, M: Me₁₂-*o*-Ph_P, N: Me₁₂-H₈, O: Me₁₂-*o*-Ph_{As(ax)}, P: H-*o*-Ph_{As(ax)}, Q: H-*o*-Ph_{As(eq)}, R: H_a-*o*-Ph_P, S: Me₁₅-*o*-Ph_{As(ax)}, T: Me₁₄-*o*-Ph_{As(eq)}, U: H₁₁-H₈, V: H₃₀-*o*-Ph_P, W: H₃₀-H₃₁, X: H₃₀-H₂

4.2.6.2 Single Crystal X-ray Diffraction Analysis

The molecular structure and the absolute stereochemistry of (*S_C,S_C,R_P*)-**176** were determined by single crystal X-ray diffraction analysis. Figure 4.22 shows the ORTEP drawing of the molecule. Selected bond lengths and angles are listed in Table 4.9. The 5-membered organometallic ring containing the palladium atom has asymmetric skew conformation of λ helicity with the methyl substituent on the stereogenic carbon of *S* absolute configuration occupying the axial site. Similar to the previous complexes, the P and As donor atoms of the new hetero-bidentate ligand are bonded regiospecifically to the palladium atom, with the softer phosphorus donor oriented *trans* to the nitrogen group. On the other hand, the new As-P bidentate chelate adopts the asymmetric skew conformation of λ helicity with the methyl substituent on the stereogenic C(28) of *S* absolute configuration occupying the axial position. All the substituents at C(28) and at arsenic adopt a staggered orientation (Figure 4.23) while the phenyl groups of arsenic are in pseudo-staggered orientation with respect to the methyl groups of nitrogen (Figure 4.20). The inter-chelate repulsion between the phosphino group and the naphthalenic group is larger, as shown by the angle N(1)-Pd(1)-P(1) of [174.4(1)°], than the corresponding repulsion between the AsPh₂ and NMe₂ groups with an angle N(1)-Pd(1)-As(1) of [99.8(1)°]. This huge angle between the phosphorus and the naphthylenic carbon is due to the sterically bulky *cis* propenyl group on phosphorus. The Pd(1)-As(1) bond length of 2.46(0)Å is longer than the Pd(1)-P(1) bond [2.26(0)Å]. The C(28)-C(29) bond [1.56(1)Å] is consistent with a C-C single bond distance and all the angles around C(28) are consistent of a tetrahedral carbon.

Figure 4.22. Molecular structure and absolute configuration of the cationic complex (S_C, S_C, R)

Table 4.9. Selected bond lengths (Å) and angles (°) for complex (*S_C*,*S_C*,*R_P*)-176

Pd1-P1	2.257(1)	P1-Pd1-As1	84.7(1)
Pd1-As1	2.460(1)	C1-Pd1-P1	95.1(1)
Pd1-N1	2.141(4)	C1-Pd1-As1	177.3(1)
Pd1-C1	2.057(4)	N1-Pd1-P1	174.4(1)
As1-C15	1.931(5)	C1-Pd1-N1	80.5(2)
As1-C21	1.944(5)	N1-Pd1-As1	99.8(1)
As1-C28	1.965(6)	C28-As1-Pd1	104.6(1)
P1-C30	1.812(5)	C29-P1-Pd1	110.4(2)
P1-C33	1.834(6)	C29-C28-As1	103.4(4)
P1-C29	1.854(5)	C27-C28-As1	112.4(4)
C27-C28	1.529(9)	C28-C29-P1	113.4(3)
C28-C29	1.557(8)	C27-C28-C29	113.4(5)
C30-C31	1.315(9)	C30-C31-C32	128.1(6)

Figure 4.23. Newman projection of (*S_C*,*S_C*,*R_P*)-176 on C(28) and As(1)

4.2.6.3 Stereochemistry of the Formation of the Diastereomers

The *cis* geometry of the propenyl phosphine allows the arsenide to lie just below the electrophilic carbon whenever the transition state is in the λ conformation (Figure 4.24). This arrangement makes the formation of the new As-C bond less sterically hindered by the methyl group in contrast when the propenyl group is in *trans* geometry. This addition retains the methyl group in its axial position, which eventually experience a small 1,3-diaxial repulsion with the axially oriented phenyl or propenyl group of the phosphorus atom. This is evidently confirmed by the larger C(30)-P(1)-C(33) angle [106.2(2)°] of the (*S_C,S_C,R_P*)-**176** from the *cis* isomer compared to the angle [103.1(3)°] of (*S_C,R_C,S_P*)-**172** from the *trans* isomer.

Similar to the previous diastereomers from *trans* propenyl, (*S_C,S_C,S_P*)-**176** and (*S_C,S_C,R_P*)-**176** in Figure 4.18, these complexes' As-P bidentate ring exist in λ conformation giving lesser inter-chelate repulsion and both only differ in the configuration of the stereogenic phosphorus. The latter two diastereomers, (*S_C,R_C,S_P*)-**176** and (*S_C,R_C,R_P*)-**176**, both have δ conformation wherein the two inter-chelate ring experience severe repulsion due to the methyl and phenyl groups of nitrogen and arsenic, respectively. All these four complexes have their methyl group in the stereogenic carbon backbone in axial orientation.

The asymmetric hydroarsination reactions of the *cis* and the *trans* isomers have similarity in their stereoselectivity in that they both have their pairs of major and minor isomers present in almost equal ratio. This is true because similar to the *trans* isomer, the *cis* isomer of the monodentate phosphine is also capable of rotating around its Pd-P coordination bond, hence, causing an almost equal opportunity for the two major diastereomers to form.

Figure 4.24. Reaction pathways for asymmetric hydroarsination of di-1-propenyl-(Z)-phenylphosphine with diphenylarsine

4.3 Conclusion

In summary, we have demonstrated that transition metal complex-promoted asymmetric hydroarsination is a potential synthetic route for the preparation of asymmetric arsenic ligands. The 5-membered ring formed by the bidentate As-P ligand and the metal exists in a single stable conformation in solid and solution form as shown by X-ray crystallography and 2D ^1H - ^1H ROESY NMR spectroscopy. Therefore, the source of diastereomerism of the products consisting of the organopalladium complex and the As-P bidentate ligand is from the relative configuration of the newly created chiral carbon and phosphorus. In addition, the arsenic atom of the addition products remains in *cis* position relative to nitrogen. There are 4 diastereomers that resulted from the asymmetric hydroarsination reaction between diphenylarsine and *cis/trans* dipropenylphenylphosphine. We saw that the two major isomers were present at almost equal ratio due to the free rotation of the monodentate phosphine complex around its Pd-P bond. Generally, the chiral bidentate ligands can be easily liberated by treatment of the organic solution with aqueous potassium cyanide.

4.4 Experimental Section

4.4.1 Instrumentation

Please refer to Section 2.4.1.

4.4.2 Reagents

All solvents used for synthesis of ligands and reactions were deoxygenated using a positive pressure of argon. Analytical grade chemicals were purchased from Sigma-Aldrich and Strem Chemicals. The chiral palladium complexes bis(μ -chloro)bis[(*R/S*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*]dipalladium(II) (*S_C/R_C*)-**58**⁵⁰, the tertiary phosphines, diphenylvinylphosphine⁵⁴, diphenyl-1-propynylphosphine, di-1-propynylphenylphosphine and (*E*)-propenyldiphenylphosphine¹⁰⁸ were prepared according to literature methods. Divinylphenylphosphine ligand was prepared by the modification of a reported method.⁵⁴

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

4.4.3 Syntheses

Preparation of diphenylarsine

The triphenylarsine (30 g, 98 mmol) was dissolved in liquid ammonia (300 mL) and sodium metal (5 g, 220 mmol) was added slowly to the solution. After stirring overnight half of the solvent had evaporated and the solution turned orange. A saturated solution of ammonium chloride was added slowly into the solution. The solution was then extracted using diethyl ether and dried over magnesium sulfate. Following filtration, the solvent was removed under vacuum. The crude product was purified by distillation to give diphenylarsine as a colorless slightly viscous liquid: 18 g (79% yield), bp 97-98 °C at 0.2 mmHg.

Preparation of divinylphenylphosphine

Vinylbromide (6 mL, 90 mmol) was added slowly to dry magnesium turnings (2.20 g, 90 mmol) in THF (100 mL). The Grignard mixture was left stirring at room temperature for 1 h. The solution was then added dropwise to a solution of dichlorophenylphosphine (5 mL, 36 mmol) in THF (100 mL) at -78 °C (dry ice-acetone mixture). The reaction mixture was allowed to reach ambient temperature and stirred overnight. The solvent was then removed by distillation. The residue was dissolved in diethyl ether (100 mL) and then treated with aqueous ammonium chloride solution. The organic layer was separated and dried over magnesium sulfate. The solvent was removed completely and the residue (orange oil) was distilled under reduced pressure. The product

was obtained as colorless viscous oil: 3.50 g (60% yield), bp 90-91 °C at 0.5 mmHg. ^{31}P NMR (CDCl_3): δ -16.0 (s). ^1H NMR spectrum is similar to previous reports.^{47, 109}

Preparation of the di-1-propenyl-(*E*)-phenylphosphine

The preparation of this ligand was carried out based on the procedure in the literature.¹¹⁰ A solution of *E*-1-bromo-1-propene (10 g, 43 mmol) in THF was added slowly to dry magnesium turnings (2 g). The solution was left stirring until all the magnesium was consumed. The solution was then added to a solution of dichlorophenylphosphine (6 g) in THF at -78 °C. The solution was left stirring overnight. The solvent was removed under vacuum and a saturated solution of ammonium chloride was added to the residue. Diethyl ether was added and the organic layer was extracted and dried over magnesium sulfate. The solvent was then removed and the resulting residue distilled to give the product as a colorless liquid: 1.5 g (24% yield), bp 64-67 °C at 0.5 mmHg. ^{31}P NMR (CDCl_3) δ -20.1 (s) [*EE*], -57.0 (s) [*ZZ*], -38.7 (s) [*EZ*] with a ratio 7:1:2.

Preparation of the di-1-propenyl-(*Z*)-phenylphosphine

This ligand was prepared in similar manner to di-1-propenyl-(*E*)-phenylphosphine. A solution of *Z*-1-bromo-1-propene (8 g) in THF was added slowly to dry magnesium turnings (1.6 g). The solution was left stirring until all the magnesium was consumed. The solution was then added to a solution of dichlorophenylphosphine in THF at -78 °C. The solution was left stirring overnight. After 1 day the solvent was removed under vacuum and a saturated solution of ammonium chloride was added to the mixture. Diethyl ether

was added and the organic layer was extracted and dried over magnesium sulfate. The solvent was removed and the resulting residue distilled to give the product as a colorless liquid: 2.4 g (48% yield), bp 70-71 °C at 0.5 mmHg. ^{31}P NMR (CDCl_3) δ -20.1 (s) [*EE*], -57.0 (s) [*ZZ*], -38.7 (s) [*EZ*] with a ratio 1:45:6

Hydroarsination Reaction: Isolation of [(*S*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-*C,N*][1-diphenylarsino-2-diphenylphosphinoethane-*P,As*]palladium(II) hexafluorophosphate, (*S_C*)-154a

A solution of (*S_C*)-**152a** (0.30 g, 0.6 mmol) in dichloromethane was treated with an excess amount of AgPF_6 (0.14 g, 0.6 mmol) in minimum amount of water. The solution was stirred at room temperature for 1 hour. The cationic complex was then washed with water to remove excess silver salt present, after which the solution was dried with magnesium sulfate. After filtration, the solvent was removed under vacuum and the complex re-dissolved in methanol. Diphenylarsine (0.13 g, 0.6 mmol) in methanol was added slowly in the solution at room temperature during which a change of color from light yellow to light orange was observed. The mixture was then heated to 65 °C upon which white precipitate formed. The reaction was left stirring overnight. Solvent was removed and the residue purified by column chromatography using ethyl acetate/hexane and dichloromethane/hexane as eluents. After purification of the product it was re-dissolved in dichloromethane wherein diethyl ether was slowly added, crystallizing the product as colorless rectangular crystals (*S_C*)-**154a**: 0.18 g (37% yield) $[\alpha]_{\text{D}} +55.44$ (*c* 0.2, CH_2Cl_2) mp 234-236 °C ^{31}P NMR (CD_3CN , 500 MHz): δ 61.1 (s), -143.2 (sp). ^1H NMR: δ 1.95 (d, 3H, $^3J_{\text{H-H}}=6.5$ Hz, *CHMe*), 2.36-2.48 (m, 1H, *AsCHH'*), 2.52-2.59 (m, 1H, *PCH'H*), 2.61-2.67 (m,

1H, AsCHH'), 2.78 (d, 3H, $^4J_{H-P}=1.5$ Hz, NMe_{ax}), 2.86 (d, 3H, $^4J_{P-H}=4.0$ Hz, NMe_{eq}), 4.60 (qn, 1H, $^3J_{H-H}=^4J_{H-P}=6.5$ Hz, CHMe), 6.90 (dd, 1H, $^3J_{H-H}=8.5$ Hz, $^4J_{H-P}=5.5$ Hz, H₂), 7.09 (d, 1H, $^3J_{H-H}=8.5$ Hz, H₃), 7.39-7.85 (m, 22H, aromatics), 8.19-8.23 (m, 2H, *o*-Ph_p).

Isolation of [(S)-1-[1-(dimethylamino)ethyl]-2-naphthyl-C,N][(R/S)-1-diphenylarsino-2-phenylvinylphosphinoethane-P,As]palladium(II) perchlorate, (S_C,S_P/R_P)-154b****

A solution of (S_C)-**152b** (0.50 g, 1.0 mmole) in dichloromethane (50 mL) was treated with AgClO₄ (0.50 g, 2.4 mmoles) in water (5 mL). The solution was stirred for 1 hour at room temperature. The white precipitate, silver chloride, was filtered off using Celite. The solution was subsequently washed with water (3 × 30 mL) and the organic layer dried over magnesium sulfate. After filtration, the solvent was removed and the residue re-dissolved in methanol (125 mL). The solution was treated with diphenylarsine (0.23 g, 1.0 mmole) dissolved in methanol (10 mL). The reaction was stirred at room temperature for 3 days. The reaction was monitored by ³¹P NMR spectroscopy. The solvent was removed and the residue was re-dissolved in

dichloromethane. Slow addition of diethyl ether crystallized out the less soluble minor diastereomer (S_C, S_P)-**154b** as colorless needle-like crystals: 0.13 g (17% yield) $[\alpha]_D^{25} +38.2$ (c 0.1, CH_2Cl_2) mp 214-217 °C Anal. Calcd. for $\text{C}_{36}\text{H}_{38}\text{AsClINO}_4\text{PPd} \cdot 1.0 \text{CH}_2\text{Cl}_2$: C, 50.4; H, 4.6; N, 1.6. Found: C, 51.2; H, 4.8; N, 1.7. ^{31}P NMR (CDCl_3 , 300 MHz): δ 59.1 (s). ^1H NMR (CDCl_3): δ 1.73-1.84 (m, 1H, PCH_aH_b), 2.07 (d, 3H, $^3J_{\text{H-H}}=6.3$ Hz, CHMe), 2.34-2.46 (m, 1H, PCH_aH_b), 2.58-2.80 (m, 1H, AsCH_cH_d), 2.70 (s, 3H, NMe_{ax}), 2.94 (d, 3H, $^4J_{\text{P-H}}=3.6$ Hz, NMe_{eq}), 2.96-3.10 (m, 1H, AsCH_cH_d), 4.55 (qn, 1H, $^3J_{\text{H-H}}=^4J_{\text{P-H}}=6.2$ Hz, CHMe), 6.61-6.81 (m, 2H, PCHCH_2), 6.93-7.03 (m, 1H, PCHCH_2), 7.09 (dd, 1H, $^3J_{\text{H-H}}=8.4$ Hz, $^4J_{\text{P-H}}=5.7$ Hz, H_χ), 7.23 (d, 1H, $^3J_{\text{H-H}}=8.4$ Hz, H_δ), 7.36-7.79 (m, 19H, aromatics). The yellow precipitate that remained in the flask was analyzed by NMR spectroscopy. (S_C, R_P)-**154b**: 0.29 g (37% yield) ^{31}P NMR (CDCl_3 , 500 MHz): δ 56.0 (s). ^1H NMR (CDCl_3): δ 1.96 (d, 3H, $^3J_{\text{H-H}}=6.0$ Hz, CHMe), 1.98-2.07 (m, 1H, PCH_aH_b), 2.21-2.29 (m, 1H, PCH_aH_b), 2.49-2.67 (m, 2H, AsCH_cH_d), 2.80 (s, 3H, NMe_{ax}), 2.89 (d, 3H, $^4J_{\text{P-H}}=3.0$ Hz, NMe_{eq}), 4.54 (qn, 1H, $^3J_{\text{H-H}}=^4J_{\text{P-H}}=6.0$ Hz, CHMe), 6.12-6.29 (m, 2H, PCHCH_2), 6.74 (ddd, 1H, PCHCH_2), 6.90 (dd, 1H, $^3J_{\text{H-H}}=8.5$ Hz, $^4J_{\text{P-H}}=5.5$ Hz, H_χ), 7.25 (d, 1H, $^3J_{\text{H-H}}=8.5$ Hz, H_δ), 7.38-7.76 (m, 17H, aromatics), 8.03 (dd, 2H, $^3J_{\text{H-H}}=5.0$ Hz, $^3J_{\text{P-H}}=10.0$ Hz, $o\text{-Ph}$).

(S_C, S_P)-**154b** (S_C, R_P)-**154b**

Liberation of 1-diphenylarsino-2-phenylvinylphosphinoethane, (*S_P*)-158

A solution of (*S_C,R_P*)-**154b** (0.04 g, 0.05 mmole) in dichloromethane (50 mL) was treated with conc. HCl (25 mL) and stirred vigorously at room temperature for 2 hours. The organic layer was then washed with water (3 × 30 mL) and dried over magnesium sulfate. After filtration, the organic layer was reduced to give a yellow solid, (*R_P*)-**157**: 0.02 g (89% yield) [α]_D -38.5 (*c* 0.1, CH₂Cl₂). ³¹P NMR (CDCl₃, 300 MHz): δ 63.9 (s). ¹H NMR (CDCl₃): δ 2.25-2.70 (br. m, 4H, AsCH₂CH₂P), 6.18-6.45 (br. m, 2H, PCHCH₂), 6.70-6.90 (br. m, 1H, PCHCH₂), 7.43-8.30 (br. m, 15H, aromatics).

(*R_P*)-**157** in deoxygenated dichloromethane was treated with excess aqueous KCN (1 g) solution to liberate the ligand. After washing the solution with water (3 × 20 mL) the solvent was removed to give a colorless oil (*S_P*)-**158**: 0.02 g (84% yield) [α]_D -17.8 (*c* 0.16, CH₂Cl₂). ³¹P NMR (CDCl₃): δ -16.1 (s). ¹H NMR (CDCl₃, 300 MHz): δ 1.89-2.00 (m, 2H, AsCH₂), 2.01-2.11 (m, 2H, PCH₂), 5.68 (ddd, 1H, ²J_{H-H}=13.3 Hz, ³J_{H-P}=18.3 Hz, ³J_{H-H}=1.9 Hz, PCHCH'H'), 5.86 (ddd, 1H, ²J_{H-H}=11.8 Hz, ³J_{H-P}=30.6 Hz, ³J_{H-H}=1.9 Hz, PCHCH''H') 7.30-7.50 (m, 15H, aromatics).

Isolation of [(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-*C,N*][(*R*)-1-diphenylarsino-2-phenylvinylphosphinoethane-*P,As*]palladium(II) perchlorate, (*R_C,R_P*)-154

After the isolation of the less soluble isomer (*S_C,S_P*)-**154b**, the mother liquor rich with the major isomer (*S_C,R_P*)-**154b** (0.25 g, 0.3 mmole) was treated with excess aqueous KCN (2 g) solution and the organic layer was subsequently washed with diluted H₂SO₄ (0.5 M) and water. A solution of (*R_C*)-**58** (0.11 g, 0.2 mmole) in

dichloromethane and excess AgClO_4 in water is then added to yield the (R_C, R_P)-**154**. Slow addition of diethyl ether in the dichloromethane solution of this epimer resulted in its crystallization as colorless needle-like prisms: 0.17 g (82% yield). $[\alpha]_D -38.5^\circ$ (c 0.1, CH_2Cl_2) mp 214-216 $^\circ\text{C}$ ^{31}P NMR (CDCl_3 , 500 MHz): δ 59.1 (s). ^1H NMR (CDCl_3): δ 1.73-1.78 (m, 1H, PCH_aH_b), 2.05 (d, 3H, $^3J_{\text{H-H}}=6.0$ Hz, CHMe), 2.31-2.39 (m, 1H, PCH_aH_b), 2.59-2.73 (m, 1H, AsCH_cH_d), 2.67 (s, 3H, NMe_{ax}), 2.92 (d, 3H, $^4J_{\text{P-H}}=3.0$ Hz, NMe_{eq}), 2.94-3.02 (m, 1H, AsCH_cH_d), 4.55 (qn, 1H, $^3J_{\text{H-H}}=^4J_{\text{P-H}}=6.0$ Hz, CHMe), 6.62-6.75 (m, 2H, PCHCH_2), 6.93-7.01 (m, 1H, PCHCH_2), 7.06 (dd, 1H, $^3J_{\text{H-H}}=8.2$ Hz, $^4J_{\text{P-H}}=5.8$ Hz, H_χ), 7.20 (d, 1H, $^3J_{\text{H-H}}=8.5$ Hz, H_δ), 7.34-7.78 (m, 19H, aromatics).

Isolation of [(*S*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-*C,N*][1-diphenylphosphino-2-diphenylarsinopropene-*P,As*]palladium(II) hexafluorophosphate, (*S_C*)-161****

To the naphthyl palladium(II) dimer (*S_C*)-**58** (0.50 g, 0.7 mmole) in dichloromethane was added diphenyl-1-propynylphosphine (0.33 g, 1.5 mmole) to obtain the monomeric complex, (*S_C*)-**159a**. This monomeric unit was immediately treated with AgPF_6 (0.37 g, 1.5 mmole) in water. After washing off the excess silver salt, the diphenylarsine (0.34 g, 1.5 mmole) in dichloromethane was added slowly. The mixture was left stirring at room temperature for 24 hours until the reaction was complete. A yellow solid was obtained after removal of the solvent from the reaction pot, (*S_C*)-**161**: 0.21 g (16% yield) ^{31}P NMR (CDCl_3 , 300 MHz): δ 52.3 (s), -143.5 (sp). ^1H NMR (CDCl_3): δ 1.82 (d, 3H, $^3J_{\text{H-H}}=6.3$ Hz, CHMe), 2.19 (s, 3H, AsCMe), 2.78 (d,

3H, $^4J_{\text{H-P}}=1.5$ Hz, NMe_{eq}), 2.93 (d, 3H, $^3J_{\text{H-P}}=3.9$ Hz NMe_{ax}), 4.51 (qn, 1H, $^3J_{\text{H-H}}=^4J_{\text{P-H}}=6.3$ Hz, CHMe), 6.90 (dd, 1H, $^3J_{\text{H-H}}=8.4$ Hz, $^4J_{\text{P-H}}=6.0$ Hz, H_γ), 7.03 (dd, 1H, $^2J_{\text{H-P}}=12.0$ Hz, $^4J_{\text{H-H}}=1.2$ Hz, PCHCMe), 7.17 (d, 1H, $^3J_{\text{H-H}}=8.5$ Hz, H_δ), 7.38-7.85 (m, 24H, aromatics).

Isolation of dichloro-1-diphenylphosphino-2-diphenylarsinopropene-*P,As*]palladium(II), **162**

The (*S_C*)-**161** complex (0.07 g, 0.1 mmole) in dichloromethane was treated with concentrated HCl solution (20 mL) for 3 hours at room temperature. This solution was then extracted using dichloromethane. The extract was washed with water (3 × 30 mL) and dried over magnesium sulfate. After filtration, the solvent was reduced and then diethyl ether was slowly added to facilitate crystallization of the complex, which was obtained as yellow micro-crystals sparingly soluble in dichloromethane, **162**: 0.04 g (71% yield). mp 301-302 °C ^{31}P NMR (CDCl_3 , 300 MHz): δ 63.7 (s). ^1H NMR (CDCl_3): δ 2.32 (s, 3H, AsCMe), 6.85 (d, 1H, $^2J_{\text{H-P}}=14.9$ Hz, PCH), 7.50-7.80 (m, 20H, aromatics).

Isolation of [(*S*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-*C,N*][(*R/S*)-1-diphenylphosphino-2-diphenylarsinopropane-*P,As*]palladium(II) perchlorate, (*S_C*,*S_O/R_C*)-**165**

A solution of (*S_C*)-**163** (0.25 g, 0.4 mmole) in dichloromethane (50 mL) was treated with excess AgClO_4 in water (5 mL). The solution was stirred for 1 hour at room temperature. The white precipitate, silver chloride, was filtered off using Celite.

The solution was subsequently washed with water (3×30 mL) then the organic layer was dried over magnesium sulfate. The solvent was removed and the yellow solid was re-dissolved in methanol (150 mL). This solution was treated with diphenylarsine (0.10 g, 0.4 mmole) dissolved in methanol (10 mL). The reaction was stirred in room temperature for 24 hours. The crude product was monitored by ^{31}P NMR until no more starting material was present. Two new signals were observed at δ 51.17 and 51.44 with relative intensities of 1:8, respectively. The methanol was removed from the reaction pot and the crude product was re-dissolved in dichloromethane until the solution is saturated. The two products were separated by slow re-crystallization using diethyl ether. The major isomer, (S_C, R_C)-**165** crystallized as colorless square plates: 0.13 g (39% yield). $[\alpha]_D +56.8^\circ$ (c 0.2, CH_2Cl_2) mp 210-211 $^\circ\text{C}$. Anal. Calcd. for $\text{C}_{41}\text{H}_{42}\text{AsClNO}_4\text{PPd} \cdot 0.5 \text{CH}_2\text{Cl}_2$: C, 55.2; H, 4.8; N, 1.6. Found: C, 54.8; H, 4.8; N, 1.6. ^{31}P NMR (CDCl_3): δ 51.4 (s). ^1H NMR (CDCl_3 , 300 MHz): δ 1.22 (d, 3H, $^3J_{\text{H-H}}=6.6$ Hz, AsCHMe), 2.03 (d, 3H, $^3J_{\text{H-H}}=6.3$ Hz, CHMe), 2.14 (dt, 1H, $^2J_{\text{H-P}}=14.4$ Hz, $^3J_{\text{H-H}}=5.7$ Hz, PCH_aH_b), 2.40-2.50 (br. m, 1H, AsCHMe), 2.70 (s, 3H, NMe_{ax}), 2.90 (d, 3H, $^4J_{\text{P-H}}=3.6$ Hz, NMe_{eq}), 3.06 (dt, 1H, $^2J_{\text{H-P}}=14.1$ Hz, $^3J_{\text{H-H}}=4.2$ Hz, PCH_aH_b), 4.56 (qn, 1H, $^3J_{\text{H-H}}=^4J_{\text{P-H}}=6.3$ Hz, CHMe), 6.86 (dd, 1H, $^3J_{\text{H-H}}=8.40$ Hz, $^4J_{\text{P-H}}=5.70$ Hz, H_α), 7.08 (d, 1H, $^3J_{\text{H-H}}=8.7$ Hz, H_β), 7.33-7.83 (m, 22H, aromatics), 8.24 (dd, 2H, $^3J_{\text{H-H}}=6.0$ Hz, $^3J_{\text{P-H}}=6.50$ Hz, $o\text{-Ph}$). After the isolation of the major isomer, the minor isomer (S_C, S_C)-**165** subsequently crystallized from the concentrated mother liquor as colorless microplates: 0.02 g (6% yield). $[\alpha]_D +64.0^\circ$ (c 0.1, CH_2Cl_2) mp 211-212 $^\circ\text{C}$ Anal. Calc. for $\text{C}_{41}\text{H}_{42}\text{AsClNO}_4\text{PPd} \cdot 0.5 \text{CH}_2\text{Cl}_2$: C, 55.2; H, 4.8; N, 1.6. Found: C, 54.8; H, 5.0; N, 1.6. ^{31}P NMR (CDCl_3): δ 51.17 (s). ^1H NMR (CDCl_3 , 500 MHz): δ 1.20 (d, 3H, $^3J_{\text{H-H}}=6.5$ Hz, AsCHMe), 2.01 (d, 3H, $^3J_{\text{H-H}}=6.0$ Hz, CHMe), 2.12 (dt, 1H, $^2J_{\text{H-P}}=14.50$ Hz, $^3J_{\text{H-H}}=5.5$ Hz, PCH_aH_b), 2.35-2.45 (br. m, 1H, AsCHMe), 2.68 (s, 3H,

NMe_{ax}), 2.88 (d, 3H, $^4J_{P-H}=4.0$ Hz, NMe_{eq}), 3.04 (dt, 1H, $^2J_{H-P,H}=14.12$ Hz, $^3J_{H-H}=3.80$ Hz, PCH_aH_b), 4.54 (qn, 1H, $^3J_{H-H}=^4J_{P-H}=6.25$ Hz, $CHMe$), 6.84 (dd, 1H, $^3J_{H-H}=8.50$ Hz, $^4J_{P-H}=5.50$ Hz, H_χ), 7.06 (d, 1H, $^3J_{H-H}=9.0$ Hz, H_δ), 7.33-7.80 (m, 22H, aromatics), 8.22 (dd, 2H, $^3J_{H-H}=6.0$ Hz, $^3J_{P-H}=6.5$ Hz, *o*-Ph).

(S_C,R_C)-165 (S_C,S_C)-165

Liberation of 1-diphenylphosphino-2-diphenylarsinopropane, (R_C)-169

The diastereomeric complex (S_C,R_C)-165 (0.03 g, 0.04 mmole) was added in dichloromethane (20 mL). This was then treated with excess potassium cyanide (1 g) in water (20 mL). The solution was stirred for 2 hours at room temperature. The aqueous layer was then separated and the organic layer washed with water (3 × 20 mL). The solution was then washed with diluted H₂SO₄ solution (3 × 15 mL, 0.5 M) to remove the naphthylamine auxiliary and then washed with water (3 × 20 mL). The solution was dried over magnesium sulfate and then filtered off. After the removal of the organic solvent, the chiral ligand (R_C)-169 was isolated as a colorless solid, 0.15 g (90% yield), $[\alpha]_D +131.0$ (*c* 0.2, CH₂Cl₂). ^{31}P NMR (CDCl₃): δ -20.5 (s). 1H NMR (CDCl₃, 300 MHz): δ 1.38 (d, 3H, $^3J_{H-H}=6.9$ Hz, $AsCHMe$), 1.97 (dt, 1H, $^2J_{H-P,H}=12.6$

Hz, $^3J_{H-H}=5.1$ Hz, PCH_aH_b), 2.25-2.35 (m, 1H, $AsCHMe$), 2.37-2.44 (m, 1H, PCH_aH_b), 7.2-7.48 (m, 20H, aromatics).

Isolation of [(S)-1-[1-(dimethylamino)ethyl]-2-naphthyl-C,N][(R/S)-1-phenyl-(1-E-propenyl)phosphino-2-diphenylarsinopropane-P,As]palladium(II) perchlorate, ($S_C,S_C/R_C,S_P/R_P$)-172

A solution of (S_C)-**170** (0.32 g, 0.6 mmole) in dichloromethane (100 mL) was treated with excess $AgClO_4$ in water (5 mL). The organic layer was separated and washed with water (3×40 mL). The solution was then dried over magnesium sulfate and then filtered. The solvent was then removed and the residue dissolved in methanol (100 mL). The solution was deoxygenated and subsequently treated with diphenylarsine (0.14 g, 0.6 mmole) in methanol (20 mL) and the solution was stirred for 2 days at room temperature. The solvent was reduced and diethyl ether was slowly added and then left for several days. The diastereomer (S_C,R_C,S_P)-**172** crystallized out as colorless square-plates: 0.11 g (23% yield) $[\alpha]_D +8.7$ (c 0.1, CH_2Cl_2) mp 238-239 °C. Anal. Calcd. for $C_{38}H_{42}AsClNO_4PPd$: C, 55.3; H, 5.1; N, 1.7. Found: C, 54.1; H, 5.3; N, 1.7. ^{31}P NMR (CD_3CN , 500 MHz): δ 47.23 (s). 1H NMR: δ 1.19 (d, 3H, $^3J_{H-H}=6.5$ Hz, $AsCHMe$), 1.69 (dt, 1H, $^2J_{H-H,P}=15.0$ Hz, H_a), 1.96 (dd, 3H, $^3J_{H-H}=6.5$ Hz, $CHMe$), 2.18 (ddd, 3H, $^3J_{H-H}=6.5$ Hz, $^4J_{H-H,P}=4.0$ Hz, $PCHCHMe$), 2.54 (d, 3H, $^4J_{H-P}=1.5$ Hz, NMe_{ax}), 2.64-2.76 (m, 2H, H_b & $AsCHMe$), 2.81 (d, 3H, $^4J_{H-P}=4.0$ Hz, NMe_{eq}), 4.57 (qn, 1H, $^3J_{H-H}=^4J_{P-H}=6.0$ Hz, $CHMe$), 6.50 (ddd, 1H, $^2J_{H-P}=16.5$ Hz, $^3J_{H-H}=11.5$ Hz, $^4J_{H-H}=1.5$ Hz $PCHCHMe$), 7.11 (dd, 1H, $^3J_{H-H}=8.5$ Hz, $^4J_{H-P}=6.0$ Hz, H_χ), 7.20 (d, 1H, $^3J_{H-H}=8.5$ Hz, H_δ), 7.30-7.43 (m, 1H, $PCHCHMe$), 7.43-7.90 (m, 19H, aromatics). After isolating the crystals the mother liquor was re-dissolved in dichloromethane and diethyl ether was slowly added. After several days crystals of

(*S_C,S_C,R_P*)-**172** as yellow rectangular prisms resulted: 0.01 g (2.9% yield) [α]_D +71.0 (*c* 0.3, CH₂Cl₂) ³¹P NMR (CD₃CN, 500 MHz): δ 47.82 (s). ¹H NMR (CD₃CN, 500 MHz): δ 1.10 (d, 3H, ³J_{H-H}=6.5 Hz, AsCHMe), 1.71 (d, 3H, ³J_{H-H}=6.5 Hz, CHMe), 1.81-1.89 (m, 1H, H_b), 1.91 (ddd, 3H, ³J_{H-H}=6.5 Hz, ⁴J_{H-H,P}=4.0 Hz, PCHCHMe), 2.53-2.62 (m, 1H, H_a), 2.64 (d, 3H, ⁴J_{H-P}=4.0 Hz, NMe_{eq}), 2.79-2.86 (m, 1H, H), 2.92 (d, 3H, ⁴J_{H-P}=1.0 Hz, NMe_{ax}), 4.56 (qn, 1H, ³J_{H-H}=⁴J_{P-H}=6.0 Hz, CHMe), 6.29 (ddd, 1H, ²J_{H-P}=15.5 Hz, ³J_{H-H}=14.5 Hz, ⁴J_{H-H}=1.7 Hz, PCHCHMe), 6.69-6.78 (m, 1H, PCHCHMe), 6.84 (dd, 1H, ³J_{H-H}=8.5 Hz, ⁴J_{H-P}=5.5 Hz, H _{α}), 7.22 (d, 1H, ³J_{H-H}=8.5 Hz, H _{β}), 7.42-7.88 (m, 17H, aromatics), 8.10 (d, 2H, ³J_{H-H,P}=12.0 Hz, ⁴J_{H-H}=1.5 Hz, *o*-Ph).

Isolation of [(*S*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-*C,N*][(*R/S*)-1-phenyl-(1-*Z*-propenyl)phosphino-2-diphenylarsinopropane-*P,As*]palladium(II) perchlorate, (*S_C,S_C,R_P*)-176****

A solution of (*S_C*)-**174** (0.80 g, 1.5 mmole) in dichloromethane (250 mL) was treated with excess AgClO₄ in water (10 mL). The organic layer was separated and washed with water (3 $\times$ 60 mL). The solution was then dried over magnesium sulfate and then filtered. The solvent was then removed and the residue re-dissolved in methanol (200 mL). The solution was deoxygenated and subsequently treated with diphenylarsine (0.35 g, 1.5 mmole) in methanol (50 mL) and the solution was stirred for 3 days at room temperature. The solvent was reduced and diethyl ether was added slowly. The diastereomer (*S_C,S_C,R_P*)-**176** crystallized out as colorless long-rectangular prism: 0.04 (3.2% yield) [α]_D +150.0 (*c* 0.14, CH₂Cl₂) mp 224-225 °C ³¹P NMR (CDCl₃, 500 MHz): δ 36.37 (s). ¹H NMR (CDCl₃, 500 MHz): δ 0.85 (d, 3H, ³J_{H-H}=7.0 Hz, AsCHMe), 1.81 (d, 3H, ³J_{H-H}=6.5 Hz, CHMe), 2.00 (ddd, 3H, ³J_{H-H}=7.0 Hz, ⁴J_{H-}

^1H , $^2\text{J}_{\text{H-P}}=1.5$ Hz, PCHCHMe), 2.46 (dd, 2H, $^2\text{J}_{\text{H-P}}=9.5$ Hz, $^3\text{J}_{\text{H-H}}=6.5$ Hz, PCH_2), 2.80 (d, 3H, $^4\text{J}_{\text{H-P}}=4.0$ Hz, NMe_{eq}), 3.03 (d, 3H, $^4\text{J}_{\text{H-P}}=1.0$ Hz, NMe_{ax}), 3.05-3.15 (m, 1H, AsCHMe), 4.54 (qn, 1H, $^3\text{J}_{\text{H-H}}=^4\text{J}_{\text{P-H}}=6.0$ Hz, CHMe), 6.36 (dd, 1H, $^2\text{J}_{\text{H-P}}=11.2$ Hz, $^3\text{J}_{\text{H-H}}=1.6$ Hz, PCHCHMe), 6.57-6.72 (m, 1H, PCHCHMe), 6.99 (dd, 1H, $^3\text{J}_{\text{H-H}}=8.5$ Hz, $^4\text{J}_{\text{H-P}}=6.5$ Hz, H_α), 7.24-7.77 (m, 18H, aromatics), 8.19 (dd, 2H, $^3\text{J}_{\text{H-P}}=12.0$ Hz, $^3\text{J}_{\text{H-H}}=2.0$ Hz, $o\text{-Php}$). After isolating the crystals, the mother liquor was re-crystallized several times to separate the remaining diastereomers. However, even after several re-crystallization cycles the crystals of (S_C, S_C, S_P) -**176** were still contaminated with a presence of a small amount of (S_C, R_C, R_P) -**176**. (S_C, S_C, S_P) -**176**: ^{31}P NMR (CDCl_3 , 500 MHz): δ 29.7 (s) ^1H NMR: 1.26 (d, 3H, $^3\text{J}_{\text{H-H}}=7.0$ Hz, AsCHMe), 1.79 (d, 3H, $^3\text{J}_{\text{H-H}}=6.0$ Hz, CHMe), 2.15-2.26 (m, 1H, H_b), 2.46 (dd, 3H, $^3\text{J}_{\text{H-H}}=5.0$ Hz, $^4\text{J}_{\text{H-H,P}}=1.5$ Hz, PCHCHMe), 2.65 (m, 1H, H_a), 2.72 (d, 3H, $^4\text{J}_{\text{H-P}}=3.5$ Hz, NMe_{eq}), 2.96 (s, 3H, NMe_{ax}), 4.52 (qn, 1H, $^3\text{J}_{\text{H-H}}=^4\text{J}_{\text{P-H}}=5.7$ Hz, CHMe), 6.49 (t, 1H, $^2,^4\text{J}_{\text{H-P,H}}=11.0$ Hz, PCHCHMe), 6.91-7.06 (m, 1H, PCHCHMe), 7.35 (d, 1H, $^3\text{J}_{\text{H-H}}=8.5$ Hz, H_δ), 7.34-7.77 (m, 18H, aromatics), 7.88 (dd, 2H, $^3\text{J}_{\text{H-P}}=12.0$ Hz, $^3\text{J}_{\text{H-H}}=7.0$ Hz, $o\text{-Php}$). (S_C, R_C, R_P) -**176** ^{31}P NMR (CDCl_3 , 500 MHz): δ 22.8 (s) ^1H NMR: 1.22 (d, 3H, $^3\text{J}_{\text{H-H}}=6.5$ Hz, AsCHMe), 2.03 (d, 3H, $^3\text{J}_{\text{H-H}}=6.5$ Hz, CHMe), 2.54 (d, 3H, $^3\text{J}_{\text{H-H}}=7.0$ Hz, PCHCHMe), 2.60 (s, 3H, NMe_{ax}), 2.92 (d, 3H, $^4\text{J}_{\text{H-P}}=4.0$ Hz, NMe_{eq}), 4.51 (qn, 1H, $^3\text{J}_{\text{H-H}}=^4\text{J}_{\text{P-H}}=5.7$ Hz, CHMe), 6.56 (dd, 1H, $^2\text{J}_{\text{H-P}}=11.5$ Hz, $^4\text{J}_{\text{H-H}}=7.2$ Hz, PCHCHMe), 7.16-7.77 (m, 20H, aromatics and PCHCHMe), 7.82 (dd, 2H, $^3\text{J}_{\text{H-P}}=12.0$ Hz, $^3\text{J}_{\text{H-H}}=7.2$ Hz, $o\text{-Php}$)

E isomer

Z isomer

Crystal Structure Determination

Please refer to Crystal structure determination on Chapter 2.

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List of Publication

A Novel Asymmetric Hydroarsination Reaction Promoted by a Chiral Organopalladium Complex

Bungabong, M. L.; Tan, K. W.; Li, Y.; Selvaratnam, S. V.; Dongol, K. G.; Leung, P.

H., *Inorg. Chem.* **2007**, 46, 4733-4736

Appendices

A1. X-ray Crystallographic Data for (S_P, S_{As})-124

A1.1 Crystal data and structure refinement for (S_P, S_{As})-124

Identification code	leung7_0m	
Empirical formula	C ₂₂ H ₂₄ As Cl ₂ P Pd	
Formula weight	571.60	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 7.3489(3) Å	$\alpha = 90^\circ$.
	b = 15.5731(5) Å	$\beta = 90^\circ$.
	c = 19.5604(7) Å	$\gamma = 90^\circ$.
Volume	2238.59(14) Å ³	
Z	4	
Density (calculated)	1.696 Mg/m ³	
Absorption coefficient	2.611 mm ⁻¹	
F(000)	1136	
Crystal size	0.35 x 0.20 x 0.10 mm ³	
Theta range for data collection	1.67 to 30.50°.	
Index ranges	-10 ≤ h ≤ 10, -9 ≤ k ≤ 22, -27 ≤ l ≤ 27	
Reflections collected	33854	
Independent reflections	6838 [R(int) = 0.0272]	
Completeness to theta = 30.50°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6838 / 0 / 246	
Goodness-of-fit on F ²	1.038	
Final R indices [I > 2σ(I)]	R1 = 0.0242, wR2 = 0.0468	
R indices (all data)	R1 = 0.0327, wR2 = 0.0532	
Absolute structure parameter	0.010(6)	
Largest diff. peak and hole	0.626 and -0.296 e.Å ⁻³	

A1.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (S_P, S_{As}) -**124**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	1475(1)	10001(1)	2490(1)	33(1)
As(1)	645(1)	8699(1)	1973(1)	34(1)
P(1)	2685(1)	9138(1)	3282(1)	32(1)
Cl(1)	2180(1)	11237(1)	3126(1)	53(1)
Cl(2)	313(1)	10798(1)	1555(1)	58(1)
C(1)	1108(3)	7869(1)	2705(1)	35(1)
C(2)	-125(3)	8110(2)	3321(1)	37(1)
C(3)	1173(3)	8525(1)	3858(1)	36(1)
C(4)	2422(4)	7806(1)	4097(1)	38(1)
C(5)	3460(4)	7529(1)	3587(1)	37(1)
C(6)	3099(3)	8044(1)	2944(1)	34(1)
C(7)	2200(4)	7428(2)	4796(2)	57(1)
C(8)	4698(4)	6770(2)	3559(2)	56(1)
C(9)	4649(4)	9536(1)	3733(1)	38(1)
C(10)	4825(4)	9487(2)	4443(1)	47(1)
C(11)	6340(5)	9814(2)	4762(2)	64(1)
C(12)	7674(5)	10190(2)	4394(2)	75(1)
C(13)	7539(5)	10252(2)	3691(2)	72(1)
C(14)	6010(4)	9933(2)	3359(2)	53(1)
C(15)	-1823(4)	8537(2)	1679(1)	46(1)
C(16)	-2964(4)	9148(2)	1563(2)	60(1)
C(17)	2104(4)	8351(2)	1203(1)	38(1)
C(18)	2148(4)	8888(2)	638(1)	47(1)
C(19)	3128(4)	8650(2)	63(1)	57(1)
C(20)	4104(5)	7895(2)	65(2)	64(1)
C(21)	4085(4)	7363(2)	631(2)	60(1)
C(22)	3071(4)	7589(2)	1201(2)	48(1)

A1.3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for (S_P, S_{As})-**124**.

Pd(1)-P(1)	2.2368(6)	P(1)-Pd(1)-Cl(2)	173.32(2)
Pd(1)-As(1)	2.3469(3)	As(1)-Pd(1)-Cl(2)	91.562(18)
Pd(1)-Cl(1)	2.3503(6)	Cl(1)-Pd(1)-Cl(2)	93.41(2)
Pd(1)-Cl(2)	2.3683(7)	C(15)-As(1)-C(17)	104.73(11)
As(1)-C(15)	1.920(3)	C(15)-As(1)-C(1)	107.29(10)
As(1)-C(17)	1.926(3)	C(17)-As(1)-C(1)	106.80(10)
As(1)-C(1)	1.958(2)	C(15)-As(1)-Pd(1)	119.19(8)
P(1)-C(9)	1.801(3)	C(17)-As(1)-Pd(1)	115.79(7)
P(1)-C(3)	1.849(2)	C(1)-As(1)-Pd(1)	102.20(7)
P(1)-C(6)	1.853(2)	C(9)-P(1)-C(3)	111.16(11)
C(1)-C(2)	1.554(3)	C(9)-P(1)-C(6)	111.09(11)
C(1)-C(6)	1.560(3)	C(3)-P(1)-C(6)	80.87(10)
C(2)-C(3)	1.559(3)	C(9)-P(1)-Pd(1)	116.82(8)
C(3)-C(4)	1.521(3)	C(3)-P(1)-Pd(1)	119.60(8)
C(4)-C(5)	1.328(4)	C(6)-P(1)-Pd(1)	111.75(8)
C(4)-C(7)	1.497(4)	C(2)-C(1)-C(6)	105.80(19)
C(5)-C(8)	1.493(3)	C(2)-C(1)-As(1)	107.82(15)
C(5)-C(6)	1.515(3)	C(6)-C(1)-As(1)	105.44(14)
C(9)-C(14)	1.384(4)	C(1)-C(2)-C(3)	105.46(18)
C(9)-C(10)	1.397(4)	C(4)-C(3)-C(2)	105.72(19)
C(10)-C(11)	1.374(4)	C(4)-C(3)-P(1)	101.82(16)
C(11)-C(12)	1.350(5)	C(2)-C(3)-P(1)	99.83(15)
C(12)-C(13)	1.383(5)	C(5)-C(4)-C(7)	128.4(2)
C(13)-C(14)	1.390(4)	C(5)-C(4)-C(3)	110.8(2)
C(15)-C(16)	1.288(4)	C(7)-C(4)-C(3)	120.2(2)
C(17)-C(22)	1.383(4)	C(4)-C(5)-C(8)	129.3(2)
C(17)-C(18)	1.387(4)	C(4)-C(5)-C(6)	110.6(2)
C(18)-C(19)	1.386(4)	C(8)-C(5)-C(6)	119.7(2)
C(19)-C(20)	1.377(5)	C(5)-C(6)-C(1)	108.69(19)
C(20)-C(21)	1.384(5)	C(5)-C(6)-P(1)	102.62(16)
C(21)-C(22)	1.386(4)	C(1)-C(6)-P(1)	96.53(14)
		C(14)-C(9)-C(10)	118.9(3)
P(1)-Pd(1)-As(1)	83.202(16)	C(14)-C(9)-P(1)	118.3(2)
P(1)-Pd(1)-Cl(1)	92.15(2)	C(10)-C(9)-P(1)	122.8(2)
As(1)-Pd(1)-Cl(1)	173.33(2)	C(11)-C(10)-C(9)	120.4(3)

C(12)-C(11)-C(10)	120.5(3)	C(18)-C(17)-As(1)	117.8(2)
C(11)-C(12)-C(13)	120.6(3)	C(19)-C(18)-C(17)	119.8(3)
C(12)-C(13)-C(14)	119.8(3)	C(20)-C(19)-C(18)	119.8(3)
C(9)-C(14)-C(13)	119.8(3)	C(19)-C(20)-C(21)	120.6(3)
C(16)-C(15)-As(1)	124.9(2)	C(20)-C(21)-C(22)	119.8(3)
C(22)-C(17)-C(18)	120.2(2)	C(17)-C(22)-C(21)	119.8(3)
C(22)-C(17)-As(1)	122.0(2)		

Symmetry transformations used to generate equivalent atoms:

A1.4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (S_P, S_{As}) -124. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Pd(1)	41(1)	22(1)	37(1)	-1(1)	0(1)	-2(1)
As(1)	39(1)	25(1)	38(1)	-3(1)	-3(1)	-1(1)
P(1)	35(1)	25(1)	34(1)	-1(1)	2(1)	-2(1)
Cl(1)	74(1)	30(1)	56(1)	-11(1)	-9(1)	-2(1)
Cl(2)	82(1)	31(1)	59(1)	6(1)	-22(1)	0(1)
C(1)	38(2)	24(1)	44(1)	1(1)	-3(1)	-3(1)
C(2)	33(1)	31(1)	48(1)	5(1)	1(1)	-2(1)
C(3)	39(2)	33(1)	36(1)	3(1)	7(1)	-1(1)
C(4)	36(1)	35(1)	42(1)	6(1)	1(1)	-4(1)
C(5)	37(1)	29(1)	45(1)	2(1)	-6(1)	-2(1)
C(6)	35(1)	27(1)	39(1)	-2(1)	2(1)	-1(1)
C(7)	50(2)	64(2)	57(2)	27(2)	4(2)	-2(2)
C(8)	57(2)	45(1)	66(2)	2(1)	-5(2)	14(1)
C(9)	36(1)	30(1)	48(1)	-9(1)	2(1)	1(1)
C(10)	49(2)	43(1)	49(2)	-6(1)	-7(1)	-3(1)
C(11)	66(2)	56(2)	71(2)	-15(2)	-25(2)	5(2)
C(12)	50(2)	57(2)	117(3)	-34(2)	-23(2)	3(2)
C(13)	41(2)	49(2)	127(3)	-22(2)	21(2)	-8(1)
C(14)	47(2)	46(1)	65(2)	-12(1)	16(1)	-7(1)
C(15)	44(2)	37(1)	58(2)	-4(1)	-7(1)	-7(1)
C(16)	41(2)	57(2)	81(2)	5(2)	-9(2)	-3(1)
C(17)	40(1)	37(1)	36(1)	-7(1)	-2(1)	-4(1)
C(18)	43(2)	49(1)	48(2)	3(1)	-1(1)	0(1)
C(19)	51(2)	74(2)	45(2)	2(2)	6(1)	-12(2)
C(20)	55(2)	76(2)	61(2)	-20(2)	21(2)	-8(2)
C(21)	59(2)	49(2)	72(2)	-14(2)	11(2)	4(2)
C(22)	57(2)	38(1)	48(2)	-7(1)	7(1)	1(1)

A1.5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)
for (S_P, S_{As})-**124**.

	x	y	z	U(eq)
H(1)	927	7274	2555	42
H(2A)	-707	7603	3508	45
H(2B)	-1059	8514	3182	45
H(3)	581	8857	4221	43
H(6)	4032	8001	2587	40
H(7A)	999	7193	4841	85
H(7B)	2376	7868	5133	85
H(7C)	3084	6982	4862	85
H(8A)	4730	6497	3999	84
H(8B)	5901	6955	3437	84
H(8C)	4259	6370	3224	84
H(10)	3912	9231	4702	56
H(11)	6447	9775	5234	77
H(12)	8692	10410	4616	89
H(13)	8470	10507	3440	87
H(14)	5900	9986	2887	63
H(15)	-2224	7977	1615	55
H(16A)	-2612	9717	1621	72
H(16B)	-4141	9020	1420	72
H(18)	1521	9406	645	56
H(19)	3127	8999	-323	68
H(20)	4781	7742	-317	76
H(21)	4750	6855	630	72
H(22)	3041	7229	1580	57

A2. X-ray Crystallographic Data for (R_C)-150**A2.1. Crystal data and structure refinement for (R_C)-150**

Identification code	leung207
Empirical formula	C ₃₉ H ₄₃ As Cl ₄ N ₂ Pd Pt
Formula weight	1057.96
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)
Unit cell dimensions	a = 11.0700(4) Å $\alpha = 90^\circ$. b = 16.1766(4) Å $\beta = 116.0880(10)^\circ$. c = 11.7926(4) Å $\gamma = 90^\circ$.
Volume	1896.61(11) Å ³
Z	2
Density (calculated)	1.853 Mg/m ³
Absorption coefficient	5.337 mm ⁻¹
F(000)	1032
Crystal size	0.30 x 0.20 x 0.20 mm ³
Theta range for data collection	2.30 to 30.55°.
Index ranges	-15 ≤ h ≤ 15, -23 ≤ k ≤ 22, -16 ≤ l ≤ 16
Reflections collected	23812
Independent reflections	8392 [R(int) = 0.0300]
Completeness to theta = 30.55°	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4150 and 0.2974
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8392 / 1 / 439
Goodness-of-fit on F ²	1.065
Final R indices [I > 2σ(I)]	R1 = 0.0264, wR2 = 0.0668
R indices (all data)	R1 = 0.0274, wR2 = 0.0677
Absolute structure parameter	0.012(4)
Largest diff. peak and hole	2.080 and -1.274 e.Å ⁻³

A2.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (R_C)-**150**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	2806(1)	1662(1)	9632(1)	14(1)
Pt(1)	2484(1)	1433(1)	6709(1)	13(1)
As(1)	2883(1)	236(1)	7946(1)	13(1)
N(1)	2000(4)	2529(3)	5604(4)	15(1)
N(2)	1829(4)	1270(3)	10718(4)	18(1)
Cl(1)	4082(1)	2112(1)	8595(1)	18(1)
Cl(2)	1522(2)	2954(1)	9088(2)	33(1)
Cl(3)	7102(4)	1905(2)	7683(3)	99(1)
Cl(4)	6823(4)	3611(2)	7188(4)	127(2)
C(1)	1227(5)	960(3)	5049(4)	15(1)
C(2)	1129(5)	122(3)	4629(5)	20(1)
C(3)	250(5)	-110(3)	3426(5)	18(1)
C(4)	-628(4)	467(3)	2556(4)	15(1)
C(5)	-1595(5)	232(4)	1339(5)	22(1)
C(6)	-2475(5)	812(4)	541(5)	25(1)
C(7)	-2384(5)	1633(4)	899(5)	27(1)
C(8)	-1468(5)	1884(3)	2050(5)	21(1)
C(9)	-557(4)	1317(4)	2940(4)	16(1)
C(10)	418(4)	1535(3)	4177(4)	15(1)
C(11)	562(5)	2418(3)	4639(5)	17(1)
C(12)	-438(5)	2596(4)	5188(6)	28(1)
C(13)	2881(5)	2573(4)	4944(5)	21(1)
C(14)	2169(6)	3325(3)	6309(5)	24(1)
C(15)	3808(5)	-622(3)	7450(5)	17(1)
C(16)	3701(6)	-1466(4)	7669(6)	25(1)
C(17)	4291(6)	-2039(4)	7173(6)	30(1)
C(18)	4961(6)	-1780(4)	6505(7)	34(1)
C(19)	5072(7)	-965(5)	6312(7)	39(2)
C(20)	4511(6)	-376(4)	6796(6)	28(1)
C(21)	1279(5)	-314(3)	7871(5)	17(1)
C(22)	1400(5)	-872(3)	8802(5)	20(1)
C(23)	268(6)	-1188(3)	8874(5)	24(1)

C(24)	-1014(6)	-923(4)	8000(5)	26(1)
C(25)	-1130(6)	-365(4)	7056(5)	27(1)
C(26)	9(5)	-66(4)	6985(5)	21(1)
C(27)	3660(5)	566(3)	9719(4)	14(1)
C(28)	4552(4)	155(3)	10730(4)	15(1)
C(29)	5232(5)	-649(3)	10716(5)	22(1)
C(30)	4873(5)	459(3)	12027(5)	18(1)
C(31)	6226(5)	547(4)	12915(5)	24(1)
C(32)	6538(6)	779(4)	14154(5)	27(1)
C(33)	5539(7)	880(4)	14530(5)	32(1)
C(34)	4193(6)	768(4)	13662(5)	26(1)
C(35)	3850(5)	579(3)	12399(4)	18(1)
C(36)	2384(5)	505(4)	11487(5)	20(1)
C(37)	1872(6)	1940(4)	11580(5)	24(1)
C(38)	402(5)	1108(4)	9843(5)	26(1)
C(39)	7668(9)	2710(9)	7042(9)	80(4)

A2.3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for (R_C)-**150**.

Pd(1)-C(27)	1.990(5)	N(2)-C(38)	1.482(6)
Pd(1)-N(2)	2.104(4)	N(2)-C(36)	1.497(7)
Pd(1)-Cl(1)	2.3536(12)	Cl(3)-C(39)	1.754(13)
Pd(1)-Cl(2)	2.4487(15)	Cl(4)-C(39)	1.780(13)
Pd(1)-As(1)	3.0713(6)	C(1)-C(10)	1.383(7)
Pt(1)-C(1)	1.989(5)	C(1)-C(2)	1.431(7)
Pt(1)-N(1)	2.124(4)	C(2)-C(3)	1.374(7)
Pt(1)-As(1)	2.3474(5)	C(3)-C(4)	1.411(7)
Pt(1)-Cl(1)	2.4128(12)	C(4)-C(5)	1.413(6)
As(1)-C(21)	1.953(5)	C(4)-C(9)	1.440(7)
As(1)-C(27)	1.954(4)	C(5)-C(6)	1.382(8)
As(1)-C(15)	1.959(5)	C(6)-C(7)	1.383(9)
N(1)-C(13)	1.493(6)	C(7)-C(8)	1.351(7)
N(1)-C(14)	1.499(7)	C(8)-C(9)	1.424(7)
N(1)-C(11)	1.507(6)	C(9)-C(10)	1.426(6)
N(2)-C(37)	1.472(7)	C(10)-C(11)	1.511(7)

C(11)-C(12)	1.536(7)	N(1)-Pt(1)-Cl(1)	94.05(12)
C(15)-C(20)	1.374(7)	As(1)-Pt(1)-Cl(1)	86.60(3)
C(15)-C(16)	1.405(8)	C(21)-As(1)-C(27)	97.9(2)
C(16)-C(17)	1.402(8)	C(21)-As(1)-C(15)	104.4(2)
C(17)-C(18)	1.364(9)	C(27)-As(1)-C(15)	118.1(2)
C(18)-C(19)	1.353(10)	C(21)-As(1)-Pt(1)	115.35(15)
C(19)-C(20)	1.389(9)	C(27)-As(1)-Pt(1)	108.26(15)
C(21)-C(22)	1.382(7)	C(15)-As(1)-Pt(1)	112.26(15)
C(21)-C(26)	1.391(7)	C(21)-As(1)-Pd(1)	95.00(14)
C(22)-C(23)	1.390(7)	C(27)-As(1)-Pd(1)	39.27(15)
C(23)-C(24)	1.405(8)	C(15)-As(1)-Pd(1)	153.10(14)
C(24)-C(25)	1.394(8)	Pt(1)-As(1)-Pd(1)	74.416(15)
C(25)-C(26)	1.388(7)	C(13)-N(1)-C(14)	107.3(4)
C(27)-C(28)	1.343(6)	C(13)-N(1)-C(11)	109.1(4)
C(28)-C(30)	1.493(7)	C(14)-N(1)-C(11)	110.8(4)
C(28)-C(29)	1.506(7)	C(13)-N(1)-Pt(1)	108.2(3)
C(30)-C(35)	1.397(7)	C(14)-N(1)-Pt(1)	116.2(3)
C(30)-C(31)	1.407(7)	C(11)-N(1)-Pt(1)	105.1(3)
C(31)-C(32)	1.397(7)	C(37)-N(2)-C(38)	108.1(4)
C(32)-C(33)	1.370(9)	C(37)-N(2)-C(36)	108.0(4)
C(33)-C(34)	1.400(8)	C(38)-N(2)-C(36)	107.7(4)
C(34)-C(35)	1.399(7)	C(37)-N(2)-Pd(1)	109.2(3)
C(35)-C(36)	1.506(7)	C(38)-N(2)-Pd(1)	107.8(3)
		C(36)-N(2)-Pd(1)	115.7(3)
C(27)-Pd(1)-N(2)	93.45(17)	Pd(1)-Cl(1)-Pt(1)	88.53(4)
C(27)-Pd(1)-Cl(1)	85.52(13)	C(10)-C(1)-C(2)	117.0(5)
N(2)-Pd(1)-Cl(1)	174.66(12)	C(10)-C(1)-Pt(1)	114.6(4)
C(27)-Pd(1)-Cl(2)	168.92(13)	C(2)-C(1)-Pt(1)	128.2(4)
N(2)-Pd(1)-Cl(2)	91.29(12)	C(3)-C(2)-C(1)	121.9(5)
Cl(1)-Pd(1)-Cl(2)	90.66(5)	C(2)-C(3)-C(4)	121.2(5)
C(27)-Pd(1)-As(1)	38.42(13)	C(3)-C(4)-C(5)	122.2(5)
N(2)-Pd(1)-As(1)	109.63(12)	C(3)-C(4)-C(9)	118.6(4)
Cl(1)-Pd(1)-As(1)	72.65(3)	C(5)-C(4)-C(9)	119.2(5)
Cl(2)-Pd(1)-As(1)	130.51(4)	C(6)-C(5)-C(4)	120.1(5)
C(1)-Pt(1)-N(1)	80.73(18)	C(5)-C(6)-C(7)	120.6(5)
C(1)-Pt(1)-As(1)	98.84(14)	C(8)-C(7)-C(6)	121.2(5)
N(1)-Pt(1)-As(1)	176.08(11)	C(7)-C(8)-C(9)	121.5(5)
C(1)-Pt(1)-Cl(1)	173.77(14)	C(8)-C(9)-C(10)	124.5(5)

C(8)-C(9)-C(4)	117.4(4)	C(25)-C(24)-C(23)	119.5(5)
C(10)-C(9)-C(4)	118.1(4)	C(26)-C(25)-C(24)	120.5(5)
C(1)-C(10)-C(9)	123.0(5)	C(25)-C(26)-C(21)	119.9(5)
C(1)-C(10)-C(11)	115.9(4)	C(28)-C(27)-As(1)	128.3(4)
C(9)-C(10)-C(11)	121.0(4)	C(28)-C(27)-Pd(1)	129.4(4)
N(1)-C(11)-C(10)	107.1(4)	As(1)-C(27)-Pd(1)	102.3(2)
N(1)-C(11)-C(12)	112.1(4)	C(27)-C(28)-C(30)	119.7(5)
C(10)-C(11)-C(12)	110.3(4)	C(27)-C(28)-C(29)	126.5(5)
C(20)-C(15)-C(16)	119.9(5)	C(30)-C(28)-C(29)	113.6(4)
C(20)-C(15)-As(1)	117.6(4)	C(35)-C(30)-C(31)	119.8(5)
C(16)-C(15)-As(1)	122.4(4)	C(35)-C(30)-C(28)	120.5(4)
C(17)-C(16)-C(15)	118.3(5)	C(31)-C(30)-C(28)	119.5(4)
C(18)-C(17)-C(16)	120.7(6)	C(32)-C(31)-C(30)	119.9(5)
C(19)-C(18)-C(17)	120.6(6)	C(33)-C(32)-C(31)	120.4(5)
C(18)-C(19)-C(20)	120.6(6)	C(32)-C(33)-C(34)	119.9(5)
C(15)-C(20)-C(19)	119.9(6)	C(35)-C(34)-C(33)	120.7(5)
C(22)-C(21)-C(26)	119.9(5)	C(30)-C(35)-C(34)	119.1(5)
C(22)-C(21)-As(1)	119.5(4)	C(30)-C(35)-C(36)	122.2(4)
C(26)-C(21)-As(1)	120.1(4)	C(34)-C(35)-C(36)	118.7(5)
C(21)-C(22)-C(23)	120.9(5)	N(2)-C(36)-C(35)	113.1(4)
C(22)-C(23)-C(24)	119.4(5)	Cl(3)-C(39)-Cl(4)	105.4(5)

Symmetry transformations used to generate equivalent atoms:

A2.4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (*R_C*)-**150**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Pd(1)	16(1)	12(1)	15(1)	1(1)	7(1)	2(1)
Pt(1)	14(1)	12(1)	11(1)	1(1)	5(1)	-1(1)
As(1)	14(1)	11(1)	13(1)	1(1)	6(1)	0(1)
N(1)	19(2)	10(2)	17(2)	1(1)	9(2)	-3(2)
N(2)	18(2)	17(3)	19(2)	3(2)	9(2)	4(2)
Cl(1)	18(1)	18(1)	15(1)	0(1)	4(1)	-6(1)
Cl(2)	48(1)	20(1)	42(1)	10(1)	28(1)	15(1)

Cl(3)	118(3)	89(2)	52(2)	11(2)	1(2)	-36(2)
Cl(4)	111(3)	63(2)	147(3)	-44(2)	3(2)	22(2)
C(1)	20(2)	12(2)	15(2)	-1(2)	9(2)	0(2)
C(2)	26(2)	9(2)	26(2)	-3(2)	13(2)	-1(2)
C(3)	25(2)	11(2)	20(2)	-1(2)	12(2)	0(2)
C(4)	13(2)	17(2)	13(2)	-1(2)	4(2)	-5(2)
C(5)	18(2)	26(3)	19(2)	-3(2)	7(2)	-7(2)
C(6)	17(2)	37(3)	15(2)	1(2)	2(2)	-7(2)
C(7)	21(2)	35(4)	19(2)	8(2)	4(2)	8(2)
C(8)	20(2)	17(3)	20(2)	-1(2)	4(2)	-1(2)
C(9)	15(2)	18(3)	16(2)	0(2)	6(2)	2(2)
C(10)	14(2)	18(3)	13(2)	0(2)	5(2)	-2(2)
C(11)	23(2)	11(2)	15(2)	0(2)	5(2)	-1(2)
C(12)	19(2)	29(3)	33(3)	-9(2)	8(2)	1(2)
C(13)	25(2)	18(3)	21(2)	1(2)	12(2)	-4(2)
C(14)	34(3)	14(3)	16(2)	-2(2)	5(2)	-3(2)
C(15)	16(2)	18(3)	18(2)	-2(2)	8(2)	1(2)
C(16)	31(3)	17(3)	32(3)	-1(2)	19(2)	-1(2)
C(17)	36(3)	17(3)	40(3)	-1(2)	20(3)	5(2)
C(18)	31(3)	30(4)	44(4)	-3(3)	18(3)	14(3)
C(19)	42(4)	39(4)	52(4)	8(3)	35(3)	14(3)
C(20)	32(3)	24(3)	34(3)	7(2)	21(3)	3(2)
C(21)	18(2)	12(2)	21(2)	-3(2)	9(2)	-4(2)
C(22)	23(2)	15(2)	23(2)	2(2)	11(2)	1(2)
C(23)	28(3)	15(3)	27(3)	2(2)	10(2)	-7(2)
C(24)	26(3)	24(3)	27(3)	-1(2)	10(2)	-7(2)
C(25)	20(2)	32(3)	27(3)	-1(2)	9(2)	-9(2)
C(26)	16(2)	24(3)	19(2)	1(2)	4(2)	-2(2)
C(27)	16(2)	17(2)	11(2)	-1(2)	7(2)	-2(2)
C(28)	9(2)	18(2)	17(2)	3(2)	5(2)	1(2)
C(29)	21(2)	17(3)	22(2)	1(2)	4(2)	7(2)
C(30)	21(2)	14(2)	17(2)	4(2)	7(2)	-1(2)
C(31)	25(3)	25(3)	18(2)	3(2)	6(2)	0(2)
C(32)	26(3)	33(3)	9(2)	2(2)	-4(2)	-9(2)
C(33)	51(4)	25(3)	14(2)	0(2)	10(2)	-1(3)
C(34)	39(3)	26(3)	15(2)	1(2)	14(2)	1(2)
C(35)	21(2)	17(3)	13(2)	1(2)	5(2)	1(2)
C(36)	17(2)	22(3)	22(2)	8(2)	8(2)	3(2)

C(37)	27(3)	24(3)	23(2)	0(2)	12(2)	6(2)
C(38)	15(2)	34(3)	30(3)	0(2)	10(2)	-1(2)
C(39)	38(4)	163(13)	42(5)	8(6)	21(4)	9(6)

A2.5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (R_C)-**150**.

	x	y	z	U(eq)
H(2)	1688	-285	5199	24
H(3)	233	-670	3175	22
H(5)	-1639	-325	1069	26
H(6)	-3149	646	-260	30
H(7)	-2976	2027	326	32
H(8)	-1431	2452	2271	25
H(11)	373	2800	3913	21
H(12A)	-1336	2407	4595	42
H(12B)	-461	3191	5329	42
H(12C)	-154	2303	5992	42
H(13A)	2790	3118	4552	31
H(13B)	2612	2144	4291	31
H(13C)	3819	2485	5556	31
H(14A)	3129	3451	6781	36
H(14B)	1767	3273	6898	36
H(14C)	1723	3772	5709	36
H(16)	3240	-1644	8141	30
H(17)	4223	-2613	7304	36
H(18)	5353	-2176	6173	41
H(19)	5537	-794	5840	47
H(20)	4614	195	6674	33
H(22)	2269	-1043	9400	24
H(23)	360	-1579	9508	29
H(24)	-1795	-1122	8051	32
H(25)	-1996	-189	6456	32
H(26)	-77	308	6332	25
H(29A)	4860	-1094	11031	33

H(29B)	6200	-601	11257	33
H(29C)	5079	-775	9850	33
H(31)	6925	449	12672	28
H(32)	7450	868	14740	32
H(33)	5760	1026	15379	38
H(34)	3506	821	13933	31
H(36A)	2268	35	10912	24
H(36B)	1862	382	11967	24
H(37A)	1454	1751	12114	36
H(37B)	1381	2420	11087	36
H(37C)	2810	2093	12113	36
H(38A)	-96	975	10331	39
H(38B)	347	642	9293	39
H(38C)	10	1601	9328	39
H(39A)	7438	2599	6145	95
H(39B)	8654	2776	7515	95

A3. X-ray Crystallographic Data for (S_C)-154a**A3.1. Crystal data and structure refinement for (S_C)-154a**

Identification code	leung62ra	
Empirical formula	C ₄₀ H ₄₀ As F ₆ N P ₂ Pd	
Formula weight	891.99	
Temperature	173(2) K=	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 12.7663(4) Å	α = 90°.
	b = 7.9957(2) Å	β = 95.168(2)°.
	c = 18.6750(6) Å	γ = 90°.
Volume	1898.51(10) Å ³	
Z	2	
Density (calculated)	1.560 Mg/m ³	
Absorption coefficient	1.497 mm ⁻¹	
F(000)	900	
Crystal size	0.20 x 0.10 x 0.10 mm ³	
Theta range for data collection	2.19 to 30.68°.	
Index ranges	-18 ≤ h ≤ 18, -11 ≤ k ≤ 11, -26 ≤ l ≤ 26	
Reflections collected	49035	
Independent reflections	10964 [R(int) = 0.0250]	
Completeness to theta = 30.68°	98.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8647 and 0.7539	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	10964 / 1 / 463	
Goodness-of-fit on F ²	1.033	
Final R indices [I > 2σ(I)]	R1 = 0.0253, wR2 = 0.0683	
R indices (all data)	R1 = 0.0284, wR2 = 0.0703	
Absolute structure parameter	0.017(5)	
Largest diff. peak and hole	0.666 and -0.403 e.Å ⁻³	

A3.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (*S_C*)-**154a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	7602(1)	3901(1)	7548(1)	25(1)
As(1)	8112(1)	3281(1)	6347(1)	32(1)
N(1)	6359(2)	5627(3)	7283(1)	33(1)
P(1)	8957(1)	2229(1)	7919(1)	23(1)
P(2)	3049(1)	9289(1)	7092(1)	55(1)
C(1)	7213(2)	4437(3)	8560(1)	27(1)
C(2)	7821(2)	4232(3)	9229(1)	31(1)
C(3)	7436(2)	4666(4)	9862(1)	36(1)
C(4)	6401(2)	5305(3)	9872(1)	38(1)
C(5)	5958(3)	5640(4)	10530(2)	53(1)
C(6)	4945(3)	6151(5)	10534(2)	64(1)
C(7)	4330(3)	6377(5)	9882(2)	65(1)
C(8)	4725(2)	6115(4)	9233(2)	50(1)
C(9)	5782(2)	5539(3)	9213(2)	36(1)
C(10)	6221(2)	5130(3)	8557(1)	30(1)
C(11)	5579(2)	5344(3)	7840(1)	37(1)
C(12)	4909(2)	3794(5)	7668(2)	48(1)
C(13)	6813(2)	7341(3)	7381(2)	42(1)
C(14)	5814(2)	5572(4)	6545(1)	45(1)
C(15)	9289(2)	854(3)	7178(1)	35(1)
C(16)	9383(2)	1890(3)	6501(1)	37(1)
C(17)	8567(2)	5151(3)	5801(1)	34(1)
C(18)	9395(2)	6102(3)	6133(1)	40(1)
C(19)	9759(2)	7490(4)	5787(2)	47(1)
C(20)	9305(3)	7927(4)	5113(2)	54(1)
C(21)	8484(3)	6987(4)	4783(2)	50(1)
C(22)	8111(2)	5599(4)	5124(1)	41(1)
C(23)	7198(2)	1879(3)	5727(1)	40(1)
C(24)	7392(3)	1491(4)	5031(2)	50(1)
C(25)	6741(3)	366(5)	4641(2)	67(1)
C(26)	5922(3)	-389(5)	4950(2)	75(1)
C(27)	5713(3)	1(5)	5647(2)	71(1)

C(28)	6344(2)	1135(4)	6031(2)	50(1)
C(29)	10130(2)	3485(3)	8134(1)	32(1)
C(30)	11138(2)	2815(4)	8108(2)	51(1)
C(31)	12005(2)	3840(7)	8244(2)	75(1)
C(32)	11881(3)	5530(6)	8386(3)	75(1)
C(33)	10894(2)	6196(5)	8418(2)	57(1)
C(34)	10012(2)	5174(4)	8284(1)	39(1)
C(35)	8800(2)	802(3)	8650(1)	28(1)
C(36)	7796(2)	210(3)	8749(2)	39(1)
C(37)	7638(2)	-887(4)	9301(2)	46(1)
C(38)	8477(3)	-1394(4)	9766(1)	52(1)
C(39)	9463(3)	-814(5)	9674(2)	67(1)
C(40)	9633(2)	274(4)	9124(2)	50(1)
F(1)	2647(4)	9420(5)	7852(2)	141(2)
F(2)	3271(3)	7365(4)	7235(2)	109(1)
F(3)	1917(2)	9052(8)	6784(2)	143(2)
F(4)	2911(3)	11217(4)	6982(3)	142(2)
F(5)	4267(3)	9592(6)	7367(2)	140(2)
F(6)	3378(3)	9097(6)	6309(2)	120(1)

A3.3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for (S_C)-**154a**.

Pd(1)-C(1)	2.043(2)	P(2)-F(3)	1.518(3)
Pd(1)-N(1)	2.1276(19)	P(2)-F(1)	1.556(3)
Pd(1)-P(1)	2.2456(5)	P(2)-F(4)	1.563(3)
Pd(1)-As(1)	2.4413(3)	P(2)-F(6)	1.563(3)
As(1)-C(23)	1.928(3)	P(2)-F(2)	1.583(3)
As(1)-C(17)	1.929(2)	P(2)-F(5)	1.611(3)
As(1)-C(16)	1.966(3)	C(1)-C(10)	1.382(3)
N(1)-C(14)	1.487(3)	C(1)-C(2)	1.420(3)
N(1)-C(13)	1.492(3)	C(2)-C(3)	1.365(3)
N(1)-C(11)	1.522(3)	C(3)-C(4)	1.418(4)
P(1)-C(35)	1.804(2)	C(4)-C(9)	1.415(4)
P(1)-C(29)	1.817(2)	C(4)-C(5)	1.422(4)
P(1)-C(15)	1.847(2)	C(5)-C(6)	1.357(5)

C(6)-C(7)	1.401(6)	C(23)-As(1)-C(17)	109.14(11)
C(7)-C(8)	1.370(5)	C(23)-As(1)-C(16)	101.89(12)
C(8)-C(9)	1.429(3)	C(17)-As(1)-C(16)	103.39(11)
C(9)-C(10)	1.430(3)	C(23)-As(1)-Pd(1)	118.21(9)
C(10)-C(11)	1.515(3)	C(17)-As(1)-Pd(1)	116.49(7)
C(11)-C(12)	1.523(4)	C(16)-As(1)-Pd(1)	105.42(7)
C(15)-C(16)	1.525(3)	C(14)-N(1)-C(13)	106.6(2)
C(17)-C(22)	1.391(3)	C(14)-N(1)-C(11)	110.40(19)
C(17)-C(18)	1.400(4)	C(13)-N(1)-C(11)	108.8(2)
C(18)-C(19)	1.385(4)	C(14)-N(1)-Pd(1)	118.29(17)
C(19)-C(20)	1.383(5)	C(13)-N(1)-Pd(1)	107.10(15)
C(20)-C(21)	1.388(5)	C(11)-N(1)-Pd(1)	105.35(14)
C(21)-C(22)	1.385(4)	C(35)-P(1)-C(29)	109.17(10)
C(23)-C(24)	1.381(4)	C(35)-P(1)-C(15)	103.85(11)
C(23)-C(28)	1.406(4)	C(29)-P(1)-C(15)	104.71(11)
C(24)-C(25)	1.386(5)	C(35)-P(1)-Pd(1)	118.36(7)
C(25)-C(26)	1.377(6)	C(29)-P(1)-Pd(1)	109.60(8)
C(26)-C(27)	1.389(7)	C(15)-P(1)-Pd(1)	110.20(8)
C(27)-C(28)	1.372(5)	F(3)-P(2)-F(1)	88.5(2)
C(29)-C(34)	1.391(4)	F(3)-P(2)-F(4)	88.9(3)
C(29)-C(30)	1.398(3)	F(1)-P(2)-F(4)	90.6(2)
C(30)-C(31)	1.382(5)	F(3)-P(2)-F(6)	87.7(2)
C(31)-C(32)	1.389(7)	F(1)-P(2)-F(6)	176.0(2)
C(32)-C(33)	1.374(5)	F(4)-P(2)-F(6)	90.7(2)
C(33)-C(34)	1.396(4)	F(3)-P(2)-F(2)	95.3(3)
C(35)-C(40)	1.386(3)	F(1)-P(2)-F(2)	88.9(2)
C(35)-C(36)	1.393(3)	F(4)-P(2)-F(2)	175.7(2)
C(36)-C(37)	1.383(4)	F(6)-P(2)-F(2)	90.2(2)
C(37)-C(38)	1.377(4)	F(3)-P(2)-F(5)	176.1(2)
C(38)-C(39)	1.366(5)	F(1)-P(2)-F(5)	95.0(2)
C(39)-C(40)	1.379(4)	F(4)-P(2)-F(5)	89.3(2)
		F(6)-P(2)-F(5)	88.9(2)
C(1)-Pd(1)-N(1)	80.84(8)	F(2)-P(2)-F(5)	86.5(2)
C(1)-Pd(1)-P(1)	94.83(6)	C(10)-C(1)-C(2)	118.6(2)
N(1)-Pd(1)-P(1)	174.61(6)	C(10)-C(1)-Pd(1)	112.32(16)
C(1)-Pd(1)-As(1)	178.59(6)	C(2)-C(1)-Pd(1)	129.07(15)
N(1)-Pd(1)-As(1)	99.95(6)	C(3)-C(2)-C(1)	121.4(2)
P(1)-Pd(1)-As(1)	84.309(15)	C(2)-C(3)-C(4)	120.8(2)

C(9)-C(4)-C(3)	118.9(2)	C(21)-C(22)-C(17)	119.4(3)
C(9)-C(4)-C(5)	119.4(3)	C(24)-C(23)-C(28)	119.8(3)
C(3)-C(4)-C(5)	121.6(3)	C(24)-C(23)-As(1)	123.1(2)
C(6)-C(5)-C(4)	121.1(3)	C(28)-C(23)-As(1)	116.9(2)
C(5)-C(6)-C(7)	119.5(3)	C(23)-C(24)-C(25)	119.3(3)
C(8)-C(7)-C(6)	121.8(3)	C(26)-C(25)-C(24)	120.5(4)
C(7)-C(8)-C(9)	119.7(3)	C(25)-C(26)-C(27)	120.7(3)
C(4)-C(9)-C(8)	118.4(2)	C(28)-C(27)-C(26)	119.0(4)
C(4)-C(9)-C(10)	118.9(2)	C(27)-C(28)-C(23)	120.6(3)
C(8)-C(9)-C(10)	122.7(3)	C(34)-C(29)-C(30)	119.7(2)
C(1)-C(10)-C(9)	121.2(2)	C(34)-C(29)-P(1)	118.61(17)
C(1)-C(10)-C(11)	118.2(2)	C(30)-C(29)-P(1)	121.6(2)
C(9)-C(10)-C(11)	120.5(2)	C(31)-C(30)-C(29)	119.4(3)
C(10)-C(11)-N(1)	106.60(18)	C(30)-C(31)-C(32)	120.6(3)
C(10)-C(11)-C(12)	110.1(2)	C(33)-C(32)-C(31)	120.4(3)
N(1)-C(11)-C(12)	111.4(2)	C(32)-C(33)-C(34)	119.6(3)
C(16)-C(15)-P(1)	109.78(17)	C(29)-C(34)-C(33)	120.3(3)
C(15)-C(16)-As(1)	107.59(16)	C(40)-C(35)-C(36)	118.3(2)
C(22)-C(17)-C(18)	120.0(2)	C(40)-C(35)-P(1)	122.94(19)
C(22)-C(17)-As(1)	124.0(2)	C(36)-C(35)-P(1)	118.73(17)
C(18)-C(17)-As(1)	116.00(18)	C(37)-C(36)-C(35)	120.8(2)
C(19)-C(18)-C(17)	120.0(3)	C(38)-C(37)-C(36)	119.9(3)
C(20)-C(19)-C(18)	119.8(3)	C(39)-C(38)-C(37)	119.6(3)
C(19)-C(20)-C(21)	120.3(3)	C(38)-C(39)-C(40)	121.1(3)
C(22)-C(21)-C(20)	120.5(3)	C(39)-C(40)-C(35)	120.3(3)

Symmetry transformations used to generate equivalent atoms:

A3.4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (*S_C*)-**154a**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^* 2U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Pd(1)	20(1)	28(1)	26(1)	2(1)	1(1)	2(1)
As(1)	37(1)	34(1)	25(1)	2(1)	3(1)	1(1)
N(1)	29(1)	31(1)	36(1)	5(1)	-1(1)	4(1)

P(1)	19(1)	26(1)	24(1)	1(1)	3(1)	2(1)
P(2)	61(1)	54(1)	46(1)	-8(1)	-7(1)	10(1)
C(1)	22(1)	27(1)	31(1)	-2(1)	2(1)	-1(1)
C(2)	25(1)	37(1)	32(1)	-2(1)	3(1)	-2(1)
C(3)	34(1)	44(1)	29(1)	-6(1)	6(1)	-9(1)
C(4)	39(1)	34(1)	42(1)	-9(1)	17(1)	-10(1)
C(5)	59(2)	54(2)	49(2)	-20(1)	26(1)	-15(1)
C(6)	65(2)	57(2)	76(2)	-26(2)	44(2)	-8(2)
C(7)	56(2)	51(2)	96(3)	-13(2)	45(2)	11(2)
C(8)	38(1)	41(1)	75(2)	1(1)	23(1)	10(1)
C(9)	30(1)	30(1)	51(1)	-4(1)	16(1)	1(1)
C(10)	23(1)	28(1)	42(1)	2(1)	6(1)	2(1)
C(11)	23(1)	41(1)	46(1)	5(1)	3(1)	8(1)
C(12)	24(1)	60(2)	58(1)	8(2)	-6(1)	-7(1)
C(13)	44(1)	31(1)	50(1)	7(1)	3(1)	-1(1)
C(14)	41(1)	51(2)	40(1)	7(1)	-6(1)	11(1)
C(15)	41(1)	31(1)	33(1)	-2(1)	7(1)	7(1)
C(16)	44(1)	38(1)	30(1)	-2(1)	11(1)	6(1)
C(17)	41(1)	32(1)	30(1)	-1(1)	9(1)	1(1)
C(18)	47(1)	38(1)	35(1)	-7(1)	6(1)	-3(1)
C(19)	51(2)	40(1)	52(2)	-9(1)	16(1)	-9(1)
C(20)	72(2)	41(2)	52(2)	4(1)	30(2)	-5(1)
C(21)	68(2)	47(2)	38(1)	12(1)	12(1)	2(1)
C(22)	46(1)	41(1)	36(1)	4(1)	6(1)	0(1)
C(23)	50(1)	31(1)	38(1)	4(1)	-5(1)	0(1)
C(24)	65(2)	45(2)	38(1)	-2(1)	-7(1)	0(1)
C(25)	93(3)	54(2)	47(2)	-5(1)	-24(2)	-4(2)
C(26)	93(3)	46(2)	77(2)	10(2)	-44(2)	-15(2)
C(27)	74(2)	53(2)	80(3)	26(2)	-28(2)	-22(2)
C(28)	52(2)	43(2)	52(2)	14(1)	-5(1)	-5(1)
C(29)	20(1)	44(1)	34(1)	4(1)	8(1)	-2(1)
C(30)	25(1)	60(2)	70(2)	3(2)	12(1)	4(1)
C(31)	21(1)	95(3)	110(3)	7(3)	14(1)	-6(2)
C(32)	37(2)	88(3)	100(3)	4(2)	8(2)	-34(2)
C(33)	48(2)	54(2)	69(2)	-1(2)	4(1)	-23(1)
C(34)	30(1)	43(1)	44(1)	-2(1)	7(1)	-7(1)
C(35)	30(1)	28(1)	27(1)	0(1)	1(1)	1(1)
C(36)	31(1)	37(1)	48(1)	6(1)	2(1)	-5(1)

C(37)	49(1)	39(2)	53(1)	5(1)	14(1)	-9(1)
C(38)	77(2)	44(2)	35(1)	11(1)	2(1)	-15(1)
C(39)	63(2)	76(3)	57(2)	35(2)	-23(1)	-13(2)
C(40)	34(1)	62(2)	51(2)	22(1)	-10(1)	-5(1)
F(1)	224(4)	135(3)	70(2)	-3(2)	36(2)	79(3)
F(2)	113(2)	68(2)	149(3)	16(2)	39(2)	24(2)
F(3)	57(1)	221(5)	144(3)	16(3)	-27(2)	-9(3)
F(4)	153(3)	56(2)	217(5)	1(2)	15(3)	3(2)
F(5)	89(2)	118(3)	201(4)	-15(3)	-56(2)	1(2)
F(6)	141(3)	153(4)	70(2)	-1(2)	24(2)	16(3)

A3.5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (*S_C*)-**154a**.

	x	y	z	U(eq)
H(2)	8511	3784	9236	37
H(3)	7866	4537	10301	43
H(5)	6378	5503	10972	63
H(6)	4655	6355	10977	76
H(7)	3619	6721	9889	79
H(8)	4299	6315	8798	60
H(11)	5112	6345	7860	44
H(12A)	5368	2831	7609	72
H(12B)	4458	3977	7222	72
H(12C)	4470	3577	8062	72
H(13A)	7347	7511	7043	63
H(13B)	7136	7464	7874	63
H(13C)	6253	8173	7290	63
H(14A)	5211	6335	6516	67
H(14B)	5569	4431	6437	67
H(14C)	6303	5914	6197	67
H(15A)	9963	275	7315	42
H(15B)	8735	-4	7083	42
H(16A)	9443	1147	6083	44

H(16B)	10018	2607	6561	44
H(18)	9707	5795	6595	48
H(19)	10319	8139	6012	56
H(20)	9556	8876	4874	64
H(21)	8176	7298	4320	60
H(22)	7549	4958	4897	49
H(24)	7967	1989	4821	60
H(25)	6860	115	4158	80
H(26)	5496	-1186	4682	90
H(27)	5140	-509	5855	85
H(28)	6204	1419	6507	60
H(30)	11226	1666	7999	61
H(31)	12691	3385	8239	90
H(32)	12482	6229	8462	90
H(33)	10813	7345	8530	68
H(34)	9327	5635	8296	47
H(36)	7214	564	8432	46
H(37)	6951	-1291	9361	55
H(38)	8372	-2142	10148	63
H(39)	10041	-1166	9995	80
H(40)	10324	664	9068	60

A4. X-ray Crystallographic Data for (S_C, S_P)-154b**A4.1. Crystal data and structure refinement for (S_C, S_P)-154b**

Identification code	leung92	
Empirical formula	C ₃₇ H ₄₀ As Cl ₃ N O ₄ P Pd	
Formula weight	881.34	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 10.3776(4) Å	$\alpha = 90^\circ$.
	b = 8.5268(4) Å	$\beta = 94.9940(10)^\circ$.
	c = 21.5771(9) Å	$\gamma = 90^\circ$.
Volume	1902.06(14) Å ³	
Z	2	
Density (calculated)	1.539 Mg/m ³	
Absorption coefficient	1.643 mm ⁻¹	
F(000)	892	
Crystal size	0.30 x 0.30 x 0.12 mm ³	
Theta range for data collection	2.26 to 30.55°.	
Index ranges	-14 ≤ h ≤ 14, -12 ≤ k ≤ 11, -30 ≤ l ≤ 30	
Reflections collected	47462	
Independent reflections	11295 [R(int) = 0.0334]	
Completeness to theta = 30.55°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8272 and 0.6385	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	11295 / 5 / 420	
Goodness-of-fit on F ²	1.048	
Final R indices [I > 2σ(I)]	R1 = 0.0435, wR2 = 0.1176	
R indices (all data)	R1 = 0.0512, wR2 = 0.1238	
Absolute structure parameter	0.016(9)	
Largest diff. peak and hole	2.199 and -1.043 e.Å ⁻³	

A4.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (S_C, S_P)-**154b**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	6480(1)	6771(1)	7658(1)	33(1)
As(1)	7611(1)	7246(1)	8679(1)	36(1)
C(1)	5536(4)	6300(5)	6804(2)	34(1)
C(2)	5891(4)	6723(6)	6202(2)	39(1)
C(3)	5179(4)	6252(6)	5681(2)	42(1)
C(4)	4056(4)	5288(6)	5710(2)	40(1)
C(5)	3326(5)	4719(7)	5176(2)	51(1)
C(6)	2291(5)	3797(7)	5215(2)	54(1)
C(7)	1882(5)	3401(7)	5793(2)	53(1)
C(8)	2540(4)	3958(6)	6347(2)	44(1)
C(9)	3670(4)	4885(5)	6308(2)	38(1)
C(10)	4436(4)	5400(5)	6848(2)	35(1)
C(11)	4033(4)	5017(6)	7479(2)	38(1)
C(12)	3111(5)	6289(7)	7682(2)	50(1)
C(13)	4937(5)	4902(7)	8584(2)	48(1)
C(14)	5949(4)	3448(6)	7799(2)	41(1)
C(15)	8289(4)	5495(5)	9175(2)	39(1)
C(16)	9141(5)	4489(7)	8894(2)	50(1)
C(17)	9599(5)	3159(8)	9224(3)	60(1)
C(18)	9204(5)	2836(7)	9796(3)	59(1)
C(19)	8386(5)	3834(7)	10066(2)	52(1)
C(20)	7927(5)	5143(6)	9766(2)	44(1)
C(21)	6754(4)	8647(5)	9212(2)	37(1)
C(22)	7310(4)	9079(6)	9796(2)	44(1)
C(23)	6736(5)	10239(7)	10135(2)	52(1)
C(24)	5613(5)	10962(7)	9886(3)	55(1)
C(25)	5054(5)	10527(7)	9314(2)	52(1)
C(26)	5620(4)	9385(6)	8972(2)	44(1)
C(27)	9121(4)	8509(6)	8520(2)	44(1)
C(28)	8660(4)	9648(6)	7997(2)	43(1)
C(29)	9214(5)	7588(7)	7013(3)	50(1)
C(30)	9262(6)	6092(9)	6898(3)	71(2)

C(31)	7347(4)	10096(5)	6806(2)	38(1)
C(32)	8255(5)	11046(7)	6556(2)	54(1)
C(33)	7820(6)	12271(8)	6164(3)	63(1)
C(34)	6517(6)	12560(6)	6032(2)	59(1)
C(35)	5629(5)	11624(7)	6289(2)	53(1)
C(36)	6033(5)	10380(6)	6675(2)	45(1)
C(37A)	7386(15)	4280(20)	4484(6)	174(14)
C(37B)	8873(1)	2919(1)	4174(1)	61(3)
Cl(1)	2225(1)	1014(1)	7996(1)	78(1)
Cl(2)	7568(1)	4244(1)	3644(1)	126(1)
Cl(3)	9025(1)	4476(1)	4798(1)	177(2)
N(1)	5259(1)	4931(1)	7917(1)	35(1)
O(1)	2282(1)	2244(1)	8410(1)	202(5)
O(2)	3482(1)	828(1)	7779(1)	92(2)
O(3)	1338(1)	1286(1)	7499(1)	183(6)
O(4)	1850(1)	-302(1)	8310(1)	118(3)
P(1)	7881(1)	8532(1)	7336(1)	36(1)

A4.3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for (S_C, S_P)-**154b**.

Pd(1)-C(1)	2.050(4)	C(28)-P(1)	1.842(5)
Pd(1)-N(1)	2.122(4)	C(29)-C(30)	1.301(9)
Pd(1)-P(1)	2.242(4)	C(29)-P(1)	1.793(5)
Pd(1)-As(1)	2.4394(5)	C(31)-C(32)	1.387(6)
As(1)-C(21)	1.929(4)	C(31)-C(36)	1.390(6)
As(1)-C(15)	1.933(4)	C(31)-P(1)	1.812(4)
As(1)-C(27)	1.956(4)	C(32)-C(33)	1.394(8)
C(1)-C(10)	1.386(5)	C(33)-C(34)	1.379(9)
C(1)-C(2)	1.427(5)	C(34)-C(35)	1.372(8)
C(2)-C(3)	1.350(6)	C(35)-C(36)	1.391(7)
C(3)-C(4)	1.432(6)	C(37A)-Cl(3)	1.784(12)
C(4)-C(5)	1.409(6)	C(37A)-Cl(2)	1.838(14)
C(4)-C(9)	1.426(6)	C(37B)-Cl(3)	1.888(14)
C(5)-C(6)	1.339(8)	C(37B)-Cl(2)	2.036(14)
C(6)-C(7)	1.393(7)	Cl(1)-O(3)	1.370(14)
C(7)-C(8)	1.407(6)	Cl(1)-O(1)	1.376(14)
C(8)-C(9)	1.423(6)	Cl(1)-O(4)	1.384(14)
C(9)-C(10)	1.422(6)	Cl(1)-O(2)	1.432(14)
C(10)-C(11)	1.495(5)		
C(11)-N(1)	1.519(4)	C(1)-Pd(1)-N(1)	80.95(11)
C(11)-C(12)	1.536(7)	C(1)-Pd(1)-P(1)	97.17(11)
C(13)-N(1)	1.505(4)	N(1)-Pd(1)-P(1)	174.3(2)
C(14)-N(1)	1.487(5)	C(1)-Pd(1)-As(1)	178.26(12)
C(15)-C(20)	1.393(6)	N(1)-Pd(1)-As(1)	97.81(3)
C(15)-C(16)	1.406(7)	P(1)-Pd(1)-As(1)	83.95(2)
C(16)-C(17)	1.400(8)	C(21)-As(1)-C(15)	108.23(18)
C(17)-C(18)	1.362(9)	C(21)-As(1)-C(27)	100.5(2)
C(18)-C(19)	1.367(8)	C(15)-As(1)-C(27)	105.3(2)
C(19)-C(20)	1.356(7)	C(21)-As(1)-Pd(1)	115.52(12)
C(21)-C(22)	1.388(6)	C(15)-As(1)-Pd(1)	119.68(13)
C(21)-C(26)	1.394(6)	C(27)-As(1)-Pd(1)	105.22(12)
C(22)-C(23)	1.395(7)	C(10)-C(1)-C(2)	118.8(4)
C(23)-C(24)	1.384(8)	C(10)-C(1)-Pd(1)	112.2(3)
C(24)-C(25)	1.368(8)	C(2)-C(1)-Pd(1)	128.9(3)
C(25)-C(26)	1.383(7)	C(3)-C(2)-C(1)	121.1(4)
C(27)-C(28)	1.534(7)	C(2)-C(3)-C(4)	121.5(4)

C(5)-C(4)-C(9)	118.9(4)	C(27)-C(28)-P(1)	109.3(3)
C(5)-C(4)-C(3)	123.0(4)	C(30)-C(29)-P(1)	123.9(5)
C(9)-C(4)-C(3)	118.1(4)	C(32)-C(31)-C(36)	120.5(5)
C(6)-C(5)-C(4)	121.9(5)	C(32)-C(31)-P(1)	119.6(4)
C(5)-C(6)-C(7)	120.4(4)	C(36)-C(31)-P(1)	119.8(3)
C(6)-C(7)-C(8)	121.1(5)	C(31)-C(32)-C(33)	118.6(5)
C(7)-C(8)-C(9)	118.6(4)	C(34)-C(33)-C(32)	121.2(5)
C(10)-C(9)-C(8)	121.9(4)	C(35)-C(34)-C(33)	119.6(5)
C(10)-C(9)-C(4)	119.1(4)	C(34)-C(35)-C(36)	120.5(5)
C(8)-C(9)-C(4)	119.0(4)	C(31)-C(36)-C(35)	119.6(5)
C(1)-C(10)-C(9)	121.3(4)	Cl(3)-C(37A)-Cl(2)	101.5(8)
C(1)-C(10)-C(11)	118.8(4)	Cl(3)-C(37B)-Cl(2)	91.2(8)
C(9)-C(10)-C(11)	119.9(4)	O(3)-Cl(1)-O(1)	111.5(8)
C(10)-C(11)-N(1)	106.9(3)	O(3)-Cl(1)-O(4)	108.8(8)
C(10)-C(11)-C(12)	109.7(4)	O(1)-Cl(1)-O(4)	107.4(8)
N(1)-C(11)-C(12)	111.4(3)	O(3)-Cl(1)-O(2)	109.4(8)
C(20)-C(15)-C(16)	119.5(5)	O(1)-Cl(1)-O(2)	107.9(8)
C(20)-C(15)-As(1)	124.0(4)	O(4)-Cl(1)-O(2)	111.9(8)
C(16)-C(15)-As(1)	116.4(3)	C(37A)-Cl(2)-C(37B)	64.9(6)
C(17)-C(16)-C(15)	118.3(5)	C(37A)-Cl(3)-C(37B)	69.1(7)
C(18)-C(17)-C(16)	120.5(6)	C(14)-N(1)-C(13)	107.5(3)
C(17)-C(18)-C(19)	120.5(5)	C(14)-N(1)-C(11)	108.9(3)
C(20)-C(19)-C(18)	121.0(5)	C(13)-N(1)-C(11)	110.6(2)
C(19)-C(20)-C(15)	120.2(5)	C(14)-N(1)-Pd(1)	106.02(17)
C(22)-C(21)-C(26)	119.2(4)	C(13)-N(1)-Pd(1)	116.9(2)
C(22)-C(21)-As(1)	121.9(3)	C(11)-N(1)-Pd(1)	106.70(17)
C(26)-C(21)-As(1)	118.5(3)	C(29)-P(1)-C(31)	106.8(2)
C(21)-C(22)-C(23)	120.0(5)	C(29)-P(1)-C(28)	103.4(2)
C(24)-C(23)-C(22)	119.8(5)	C(31)-P(1)-C(28)	101.4(2)
C(25)-C(24)-C(23)	120.3(5)	C(29)-P(1)-Pd(1)	111.28(18)
C(24)-C(25)-C(26)	120.4(5)	C(31)-P(1)-Pd(1)	121.15(14)
C(25)-C(26)-C(21)	120.3(5)	C(28)-P(1)-Pd(1)	111.04(14)
C(28)-C(27)-As(1)	106.0(3)		

Symmetry transformations used to generate equivalent atoms:

A4.4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (S_C, S_P)-**154b**. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Pd(1)	34(1)	36(1)	30(1)	1(1)	4(1)	-9(1)
As(1)	33(1)	42(1)	32(1)	2(1)	2(1)	-8(1)
C(1)	33(2)	35(2)	34(2)	1(1)	5(1)	-5(1)
C(2)	47(2)	36(2)	33(2)	3(2)	6(1)	-8(2)
C(3)	57(2)	38(2)	30(2)	5(2)	6(2)	0(2)
C(4)	48(2)	38(2)	34(2)	0(2)	1(2)	0(2)
C(5)	59(3)	55(3)	35(2)	-2(2)	-8(2)	1(2)
C(6)	59(3)	69(4)	33(2)	-4(2)	-7(2)	-7(3)
C(7)	45(2)	65(3)	46(2)	-4(2)	-9(2)	-4(2)
C(8)	36(2)	56(3)	37(2)	7(2)	-9(2)	-6(2)
C(9)	38(2)	40(2)	34(2)	3(2)	0(1)	-2(2)
C(10)	36(2)	37(2)	32(2)	4(2)	2(1)	-1(2)
C(11)	37(2)	46(2)	33(2)	8(2)	7(1)	-6(2)
C(12)	44(2)	65(3)	43(2)	1(2)	11(2)	2(2)
C(13)	54(2)	62(3)	28(2)	0(2)	5(2)	-23(2)
C(14)	44(2)	40(2)	37(2)	5(2)	-3(2)	-9(2)
C(15)	37(2)	43(2)	35(2)	1(2)	-1(1)	-6(2)
C(16)	41(2)	56(3)	52(3)	-2(2)	1(2)	0(2)
C(17)	44(2)	54(3)	80(4)	-7(3)	-4(2)	5(2)
C(18)	50(3)	51(3)	72(3)	6(3)	-16(2)	-1(2)
C(19)	47(2)	53(3)	54(3)	15(2)	-1(2)	-1(2)
C(20)	44(2)	47(3)	42(2)	2(2)	4(2)	-6(2)
C(21)	37(2)	40(2)	34(2)	3(2)	4(1)	-8(2)
C(22)	43(2)	48(3)	40(2)	-2(2)	4(2)	-1(2)
C(23)	55(3)	64(3)	39(2)	-11(2)	12(2)	-8(2)
C(24)	55(3)	60(3)	54(3)	-2(2)	20(2)	-1(2)
C(25)	51(2)	51(3)	55(3)	7(2)	13(2)	5(2)
C(26)	43(2)	49(3)	39(2)	8(2)	7(2)	0(2)
C(27)	35(2)	59(3)	37(2)	0(2)	1(2)	-18(2)
C(28)	44(2)	44(2)	40(2)	5(2)	-1(2)	-15(2)
C(29)	37(2)	52(3)	60(3)	3(2)	11(2)	-1(2)
C(30)	49(3)	75(4)	91(5)	-14(4)	18(3)	3(3)

C(31)	45(2)	34(2)	34(2)	1(2)	4(2)	-5(2)
C(32)	57(3)	53(3)	53(3)	11(2)	4(2)	-14(2)
C(33)	87(4)	52(3)	51(3)	12(2)	8(3)	-18(3)
C(34)	87(4)	38(3)	49(3)	4(2)	-6(2)	6(3)
C(35)	65(3)	40(3)	51(2)	-5(2)	-10(2)	7(2)
C(36)	51(2)	38(2)	44(2)	-4(2)	2(2)	0(2)
C(37A)	210(20)	155(17)	130(13)	121(14)	-141(15)	-161(17)
C(37B)	17(3)	103(9)	66(6)	-27(6)	19(3)	0(4)
Cl(1)	43(1)	85(1)	106(1)	41(1)	9(1)	-17(1)
Cl(2)	100(2)	134(3)	143(2)	-38(2)	7(2)	17(2)
Cl(3)	134(2)	200(4)	184(3)	112(3)	-67(2)	-52(3)
N(1)	39(2)	39(2)	28(1)	1(1)	4(1)	-12(1)
O(1)	105(5)	130(8)	386(17)	-42(10)	98(8)	-18(6)
O(2)	45(2)	104(4)	126(4)	38(4)	11(2)	-23(2)
O(3)	57(3)	329(16)	161(6)	164(9)	-7(3)	-30(5)
O(4)	62(3)	138(6)	155(6)	85(5)	19(3)	-25(3)
P(1)	34(1)	39(1)	36(1)	4(1)	5(1)	-7(1)

A4.5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (S_C, S_P)-**154b**.

	x	y	z	U(eq)
H(2)	6640	7346	6166	46
H(3)	5429	6567	5287	50
H(5)	3574	4998	4777	61
H(6)	1834	3411	4846	65
H(7)	1148	2744	5813	64
H(8)	2235	3721	6739	52
H(11)	3586	3977	7467	46
H(12A)	3514	7322	7650	76
H(12B)	2929	6102	8114	76
H(12C)	2301	6256	7413	76
H(13A)	4269	4110	8633	72
H(13B)	4616	5934	8698	72

H(13C)	5715	4642	8854	72
H(14A)	6772	3417	8058	61
H(14B)	6116	3395	7359	61
H(14C)	5414	2552	7901	61
H(16)	9398	4706	8491	60
H(17)	10191	2476	9048	72
H(18)	9498	1911	10009	71
H(19)	8136	3607	10470	62
H(20)	7356	5821	9959	53
H(22)	8083	8583	9964	53
H(23)	7113	10532	10535	63
H(24)	5229	11764	10114	66
H(25)	4273	11012	9151	62
H(26)	5234	9103	8573	52
H(27A)	9444	9093	8899	53
H(27B)	9825	7833	8390	53
H(28A)	9406	10243	7862	51
H(28B)	8037	10405	8149	51
H(29)	9928	8217	6920	59
H(30A)	8563	5433	6986	86
H(30B)	9996	5659	6726	86
H(32)	9154	10867	6650	65
H(33)	8432	12918	5984	76
H(34)	6237	13402	5765	71
H(35)	4731	11827	6202	63
H(36)	5414	9728	6848	53
H(37A)	6853	5176	4598	209
H(37B)	6997	3291	4623	209
H(37C)	8511	1919	4315	73
H(37D)	9686	2733	3977	73

A5. X-ray Crystallographic Data for (R_C, R_P)-154**A5.1. Crystal data and structure refinement for (R_C, R_P)-154.**

Identification code	leung152m
Empirical formula	C ₃₇ H ₄₀ As Cl ₃ N O ₄ P Pd
Formula weight	881.34
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)
Unit cell dimensions	a = 10.3937(4) Å $\alpha = 90^\circ$. b = 8.5340(3) Å $\beta = 94.271(2)^\circ$. c = 21.6814(9) Å $\gamma = 90^\circ$.
Volume	1917.80(13) Å ³
Z	2
Density (calculated)	1.526 Mg/m ³
Absorption coefficient	1.629 mm ⁻¹
F(000)	892
Crystal size	0.20 x 0.16 x 0.08 mm ³
Theta range for data collection	0.94 to 30.66°.
Index ranges	-14 ≤ h ≤ 14, -12 ≤ k ≤ 12, -30 ≤ l ≤ 31
Reflections collected	47717
Independent reflections	10836 [R(int) = 0.0467]
Completeness to theta = 30.66°	99.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8807 and 0.7364
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	10836 / 1 / 436
Goodness-of-fit on F ²	1.090
Final R indices [I > 2σ(I)]	R1 = 0.0463, wR2 = 0.1092
R indices (all data)	R1 = 0.0683, wR2 = 0.1352
Absolute structure parameter	0.021(12)
Largest diff. peak and hole	1.364 and -0.813 e.Å ⁻³

A5.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (R_C, R_P)-**154**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	3466(1)	219(1)	2338(1)	33(1)
As(1)	2356(1)	-255(1)	1319(1)	35(1)
P(1)	2065(1)	-1554(2)	2661(1)	36(1)
Cl(1)	7734(2)	5959(3)	1994(1)	70(1)
Cl(2)	7519(3)	7743(4)	3637(2)	105(1)
Cl(3)	9047(3)	7491(6)	4784(2)	160(2)
O(1)	7652(8)	4757(15)	1557(6)	168(5)
O(2)	8118(6)	7285(10)	1682(4)	109(3)
O(3)	6477(5)	6155(9)	2210(3)	87(2)
O(4)	8625(6)	5608(16)	2470(4)	158(6)
N(1)	4689(4)	2051(6)	2077(2)	35(1)
C(1)	4408(5)	670(6)	3190(2)	35(1)
C(2)	4033(5)	261(8)	3790(2)	40(1)
C(3)	4745(5)	719(7)	4307(2)	41(1)
C(4)	5870(5)	1671(7)	4272(2)	40(1)
C(5)	6598(6)	2231(8)	4807(3)	50(2)
C(6)	7650(6)	3152(10)	4766(3)	56(2)
C(7)	8062(6)	3537(9)	4186(3)	52(2)
C(8)	7381(5)	3013(8)	3646(3)	43(1)
C(9)	6257(5)	2075(7)	3677(2)	39(1)
C(10)	5501(5)	1577(7)	3143(2)	35(1)
C(11)	5902(5)	1957(7)	2508(2)	38(1)
C(12)	6839(5)	701(9)	2302(3)	50(2)
C(13)	4003(5)	3537(7)	2200(2)	39(1)
C(14)	5031(5)	2101(8)	1420(2)	43(1)
C(15)	1692(5)	1504(7)	827(2)	37(1)
C(16)	828(6)	2495(8)	1097(3)	45(1)
C(17)	388(6)	3830(9)	779(3)	55(2)
C(18)	797(6)	4144(9)	203(3)	56(2)
C(19)	1620(5)	3161(8)	-68(3)	49(1)
C(20)	2072(5)	1854(8)	235(3)	43(1)
C(21)	3235(5)	-1661(7)	788(2)	35(1)

C(22)	2678(6)	-2087(8)	207(2)	43(1)
C(23)	3276(6)	-3251(9)	-129(3)	52(2)
C(24)	4387(6)	-3965(9)	115(3)	56(2)
C(25)	4923(6)	-3541(9)	688(3)	51(1)
C(26)	4369(5)	-2380(7)	1030(3)	40(1)
C(27)	846(5)	-1524(8)	1480(3)	45(1)
C(28)	1301(5)	-2665(7)	1999(3)	40(1)
C(29)	729(6)	-626(9)	2989(3)	53(2)
C(30)	676(7)	885(11)	3108(4)	70(2)
C(31)	2595(5)	-3118(7)	3186(2)	37(1)
C(32)	1688(6)	-4079(8)	3446(3)	52(2)
C(33)	2115(7)	-5292(9)	3832(3)	60(2)
C(34)	3413(8)	-5572(8)	3961(3)	59(2)
C(35)	4325(6)	-4617(8)	3699(3)	53(2)
C(36)	3910(6)	-3391(7)	3316(3)	43(1)
C(37)	7560(20)	7990(30)	4435(8)	360(20)

A5.3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for (R_C, R_P)-**154**.

Pd(1)-C(1)	2.062(5)	C(18)-C(19)	1.362(10)
Pd(1)-N(1)	2.118(4)	C(19)-C(20)	1.359(9)
Pd(1)-P(1)	2.2488(14)	C(21)-C(22)	1.394(8)
Pd(1)-As(1)	2.4473(6)	C(21)-C(26)	1.397(8)
As(1)-C(21)	1.938(5)	C(22)-C(23)	1.404(9)
As(1)-C(15)	1.939(6)	C(23)-C(24)	1.377(10)
As(1)-C(27)	1.959(5)	C(24)-C(25)	1.371(10)
P(1)-C(29)	1.790(7)	C(25)-C(26)	1.388(9)
P(1)-C(31)	1.813(6)	C(27)-C(28)	1.535(8)
P(1)-C(28)	1.850(6)	C(29)-C(30)	1.317(10)
Cl(1)-O(4)	1.369(7)	C(31)-C(36)	1.395(8)
Cl(1)-O(2)	1.392(7)	C(31)-C(32)	1.399(8)
Cl(1)-O(1)	1.394(11)	C(32)-C(33)	1.384(10)
Cl(1)-O(3)	1.430(6)	C(33)-C(34)	1.378(10)
Cl(2)-C(37)	1.741(16)	C(34)-C(35)	1.401(10)
Cl(3)-C(37)	1.728(15)	C(35)-C(36)	1.384(9)
N(1)-C(13)	1.489(8)		
N(1)-C(14)	1.494(6)	C(1)-Pd(1)-N(1)	81.20(18)
N(1)-C(11)	1.515(6)	C(1)-Pd(1)-P(1)	96.95(14)
C(1)-C(10)	1.385(7)	N(1)-Pd(1)-P(1)	174.60(14)
C(1)-C(2)	1.429(6)	C(1)-Pd(1)-As(1)	178.72(15)
C(2)-C(3)	1.355(7)	N(1)-Pd(1)-As(1)	97.67(11)
C(3)-C(4)	1.431(8)	P(1)-Pd(1)-As(1)	84.13(4)
C(4)-C(5)	1.419(8)	C(21)-As(1)-C(15)	108.4(2)
C(4)-C(9)	1.421(7)	C(21)-As(1)-C(27)	100.5(3)
C(5)-C(6)	1.355(10)	C(15)-As(1)-C(27)	105.6(2)
C(6)-C(7)	1.398(9)	C(21)-As(1)-Pd(1)	115.28(15)
C(7)-C(8)	1.395(8)	C(15)-As(1)-Pd(1)	119.58(15)
C(8)-C(9)	1.422(8)	C(27)-As(1)-Pd(1)	105.12(16)
C(9)-C(10)	1.415(7)	C(29)-P(1)-C(31)	106.6(3)
C(10)-C(11)	1.504(7)	C(29)-P(1)-C(28)	103.5(3)
C(11)-C(12)	1.536(8)	C(31)-P(1)-C(28)	101.7(3)
C(15)-C(16)	1.394(8)	C(29)-P(1)-Pd(1)	111.4(2)
C(15)-C(20)	1.402(8)	C(31)-P(1)-Pd(1)	121.19(18)
C(16)-C(17)	1.391(10)	C(28)-P(1)-Pd(1)	110.66(17)
C(17)-C(18)	1.374(10)	O(4)-Cl(1)-O(2)	110.0(5)

O(4)-Cl(1)-O(1)	110.8(9)	C(10)-C(11)-C(12)	109.9(5)
O(2)-Cl(1)-O(1)	105.8(7)	N(1)-C(11)-C(12)	112.0(4)
O(4)-Cl(1)-O(3)	111.2(4)	C(16)-C(15)-C(20)	119.3(6)
O(2)-Cl(1)-O(3)	111.5(4)	C(16)-C(15)-As(1)	116.9(4)
O(1)-Cl(1)-O(3)	107.3(4)	C(20)-C(15)-As(1)	123.8(4)
C(13)-N(1)-C(14)	107.3(5)	C(17)-C(16)-C(15)	119.1(6)
C(13)-N(1)-C(11)	108.8(4)	C(18)-C(17)-C(16)	119.9(6)
C(14)-N(1)-C(11)	110.1(4)	C(19)-C(18)-C(17)	121.2(6)
C(13)-N(1)-Pd(1)	106.0(3)	C(20)-C(19)-C(18)	120.2(6)
C(14)-N(1)-Pd(1)	117.8(3)	C(19)-C(20)-C(15)	120.4(6)
C(11)-N(1)-Pd(1)	106.5(3)	C(22)-C(21)-C(26)	120.4(5)
C(10)-C(1)-C(2)	119.0(5)	C(22)-C(21)-As(1)	121.1(4)
C(10)-C(1)-Pd(1)	112.1(3)	C(26)-C(21)-As(1)	118.1(4)
C(2)-C(1)-Pd(1)	128.8(4)	C(21)-C(22)-C(23)	118.9(6)
C(3)-C(2)-C(1)	120.9(5)	C(24)-C(23)-C(22)	120.3(6)
C(2)-C(3)-C(4)	121.2(5)	C(25)-C(24)-C(23)	120.3(6)
C(5)-C(4)-C(9)	119.3(5)	C(24)-C(25)-C(26)	121.1(6)
C(5)-C(4)-C(3)	122.4(5)	C(25)-C(26)-C(21)	119.0(5)
C(9)-C(4)-C(3)	118.3(5)	C(28)-C(27)-As(1)	105.9(3)
C(6)-C(5)-C(4)	121.7(6)	C(27)-C(28)-P(1)	109.6(4)
C(5)-C(6)-C(7)	119.8(6)	C(30)-C(29)-P(1)	123.8(6)
C(8)-C(7)-C(6)	120.6(6)	C(36)-C(31)-C(32)	120.0(5)
C(7)-C(8)-C(9)	120.5(6)	C(36)-C(31)-P(1)	119.8(4)
C(10)-C(9)-C(4)	119.4(5)	C(32)-C(31)-P(1)	120.1(5)
C(10)-C(9)-C(8)	122.6(5)	C(33)-C(32)-C(31)	119.1(6)
C(4)-C(9)-C(8)	117.9(5)	C(34)-C(33)-C(32)	121.2(6)
C(1)-C(10)-C(9)	121.1(5)	C(33)-C(34)-C(35)	119.9(6)
C(1)-C(10)-C(11)	118.2(4)	C(36)-C(35)-C(34)	119.6(6)
C(9)-C(10)-C(11)	120.6(5)	C(35)-C(36)-C(31)	120.2(6)
C(10)-C(11)-N(1)	107.6(4)	Cl(3)-C(37)-Cl(2)	111.0(12)

Symmetry transformations used to generate equivalent atoms:

A5.4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (R_C, R_P)-**154**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	32(1)	38(1)	29(1)	2(1)	4(1)	-8(1)
As(1)	31(1)	42(1)	31(1)	2(1)	1(1)	-7(1)
P(1)	31(1)	40(1)	36(1)	5(1)	6(1)	-5(1)
Cl(1)	40(1)	82(1)	87(1)	29(1)	6(1)	-19(1)
Cl(2)	84(2)	121(3)	110(2)	26(2)	6(2)	-15(2)
Cl(3)	114(2)	184(4)	173(3)	-103(3)	-64(2)	53(3)
O(1)	92(5)	126(9)	293(13)	-57(10)	60(7)	-25(6)
O(2)	59(3)	125(6)	143(6)	71(5)	15(4)	-23(4)
O(3)	43(3)	105(5)	115(5)	27(4)	13(3)	-23(3)
O(4)	51(3)	285(16)	138(6)	133(9)	-2(3)	-28(5)
N(1)	33(2)	42(2)	29(2)	-3(2)	-1(2)	-13(2)
C(1)	43(3)	30(2)	31(2)	3(2)	6(2)	0(2)
C(2)	48(3)	37(2)	35(2)	6(2)	7(2)	-5(3)
C(3)	53(3)	40(3)	32(2)	5(2)	14(2)	-4(2)
C(4)	46(3)	39(3)	34(2)	-1(2)	1(2)	7(2)
C(5)	61(4)	53(4)	35(3)	1(3)	-4(3)	5(3)
C(6)	53(4)	76(5)	38(3)	-4(3)	-8(3)	-6(3)
C(7)	40(3)	64(4)	49(3)	0(3)	-11(2)	-1(3)
C(8)	36(3)	57(4)	34(3)	2(2)	-9(2)	2(2)
C(9)	43(3)	42(3)	31(2)	-1(2)	1(2)	3(2)
C(10)	35(2)	40(3)	29(2)	3(2)	2(2)	2(2)
C(11)	31(2)	51(3)	32(2)	4(2)	2(2)	-3(2)
C(12)	40(3)	72(5)	39(3)	-7(3)	8(2)	2(3)
C(13)	44(3)	38(3)	35(2)	1(2)	-3(2)	-8(2)
C(14)	43(3)	55(4)	31(2)	7(2)	3(2)	-18(3)
C(15)	32(2)	42(3)	36(2)	-4(2)	0(2)	-8(2)
C(16)	40(3)	52(4)	43(3)	-4(3)	1(2)	-4(2)
C(17)	41(3)	50(4)	73(4)	-8(3)	-3(3)	6(3)
C(18)	46(3)	53(4)	66(4)	7(3)	-15(3)	-1(3)
C(19)	37(3)	60(4)	49(3)	16(3)	-3(2)	-1(3)
C(20)	36(3)	47(3)	45(3)	4(2)	1(2)	-3(2)
C(21)	35(2)	37(3)	35(2)	3(2)	4(2)	-5(2)

C(22)	45(3)	49(3)	35(3)	1(2)	3(2)	-6(2)
C(23)	48(3)	69(4)	40(3)	-9(3)	8(2)	-12(3)
C(24)	55(4)	59(4)	56(4)	-2(3)	21(3)	-1(3)
C(25)	50(3)	55(4)	49(3)	3(3)	8(3)	8(3)
C(26)	38(3)	45(3)	38(3)	6(2)	7(2)	-2(2)
C(27)	31(2)	62(4)	40(3)	4(3)	0(2)	-20(2)
C(28)	32(2)	46(3)	41(3)	5(2)	-4(2)	-15(2)
C(29)	41(3)	55(4)	64(4)	6(3)	15(3)	-6(3)
C(30)	48(4)	74(5)	90(6)	-6(4)	25(4)	8(3)
C(31)	46(3)	35(3)	31(2)	0(2)	3(2)	-2(2)
C(32)	51(3)	54(4)	51(3)	12(3)	9(3)	-10(3)
C(33)	82(5)	50(4)	50(3)	11(3)	12(3)	-18(3)
C(34)	88(5)	40(4)	47(3)	-3(3)	-7(3)	11(3)
C(35)	64(4)	45(4)	48(3)	-9(3)	-8(3)	12(3)
C(36)	43(3)	45(3)	41(3)	-4(2)	5(2)	1(2)
C(37)	480(40)	380(30)	170(14)	-197(19)	-220(20)	390(30)

A5.5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (R_C, R_P)-**154**.

	x	y	z	U(eq)
H(2)	3273	-341	3826	48
H(3)	4492	402	4700	49
H(5)	6340	1954	5204	60
H(6)	8107	3535	5131	68
H(7)	8812	4161	4159	62
H(8)	7671	3285	3255	51
H(11)	6344	2998	2519	46
H(12A)	7588	638	2604	76
H(12B)	7125	979	1896	76
H(12C)	6401	-316	2276	76
H(13A)	3848	3596	2640	59
H(13B)	3176	3564	1951	59
H(13C)	4532	4430	2090	59

H(14A)	4257	2329	1150	65
H(14B)	5386	1086	1308	65
H(14C)	5676	2922	1373	65
H(16)	543	2262	1493	54
H(17)	-194	4522	959	66
H(18)	500	5063	-9	67
H(19)	1880	3389	-469	59
H(20)	2648	1175	44	51
H(22)	1907	-1598	42	52
H(23)	2911	-3547	-527	63
H(24)	4785	-4755	-114	67
H(25)	5685	-4051	853	61
H(26)	4757	-2079	1423	48
H(27A)	140	-852	1611	54
H(27B)	531	-2106	1104	54
H(28A)	1928	-3416	1845	48
H(28B)	556	-3265	2133	48
H(29)	17	-1259	3082	63
H(30A)	1373	1548	3019	84
H(30B)	-59	1312	3282	84
H(32)	791	-3900	3359	62
H(33)	1503	-5944	4012	72
H(34)	3690	-6411	4227	71
H(35)	5220	-4811	3783	64
H(36)	4524	-2732	3142	52
H(37A)	7363	9099	4529	429
H(37B)	6882	7330	4603	429

A6. X-ray Crystallographic Data for 162**A6.1. Crystal data and structure refinement for 162**

Identification code	leung45	
Empirical formula	C ₂₇ H ₂₄ As Cl ₂ P Pd	
Formula weight	631.65	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 13.0798(4) Å	α = 90°.
	b = 11.5713(4) Å	β = 102.363(2)°.
	c = 16.9996(7) Å	γ = 90°.
Volume	2513.23(16) Å ³	
Z	4	
Density (calculated)	1.669 Mg/m ³	
Absorption coefficient	2.335 mm ⁻¹	
F(000)	1256	
Crystal size	0.30 x 0.20 x 0.20 mm ³	
Theta range for data collection	2.37 to 30.53°.	
Index ranges	-18 ≤ h ≤ 18, -16 ≤ k ≤ 15, -22 ≤ l ≤ 24	
Reflections collected	21647	
Independent reflections	7279 [R(int) = 0.0241]	
Completeness to theta = 30.53°	99.9 %	
Absorption correction	None	
Max. and min. transmission	0.6524 and 0.5409	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7279 / 2 / 291	
Goodness-of-fit on F ²	1.055	
Final R indices [I > 2σ(I)]	R1 = 0.0190, wR2 = 0.0484	
R indices (all data)	R1 = 0.0199, wR2 = 0.0487	
Absolute structure parameter	0.033(4)	
Extinction coefficient	0.00000(6)	
Largest diff. peak and hole	0.617 and -0.264 e.Å ⁻³	

A6.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **162**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Pd(1)	-456(1)	6773(1)	8147(1)	20(1)
As(1)	891(1)	6577(1)	9269(1)	23(1)
P(1)	332(1)	8418(1)	7925(1)	19(1)
Cl(1)	-1134(1)	5003(1)	8498(1)	36(1)
Cl(2)	-1820(1)	7021(1)	7020(1)	30(1)
C(1)	1738(2)	5220(2)	9311(1)	27(1)
C(2)	1656(2)	4545(2)	8628(2)	37(1)
C(3)	2285(2)	3576(3)	8654(2)	49(1)
C(4)	2966(2)	3269(2)	9352(2)	52(1)
C(5)	3051(2)	3945(3)	10035(2)	51(1)
C(6)	2436(2)	4922(2)	10018(2)	39(1)
C(7)	498(2)	6592(2)	10295(1)	23(1)
C(8)	62(2)	5599(2)	10545(1)	34(1)
C(9)	-260(2)	5596(2)	11277(2)	40(1)
C(10)	-126(2)	6582(2)	11752(2)	39(1)
C(11)	303(2)	7559(2)	11506(1)	37(1)
C(12)	613(2)	7581(2)	10773(1)	29(1)
C(13)	2842(2)	7941(2)	9876(1)	35(1)
C(14)	1829(1)	7874(2)	9279(1)	25(1)
C(15)	1508(2)	8634(2)	8679(1)	25(1)
C(16)	805(2)	8465(2)	6985(1)	22(1)
C(17)	1470(2)	9361(2)	6862(1)	29(1)
C(18)	1865(2)	9395(2)	6173(1)	34(1)
C(19)	1598(2)	8546(2)	5590(2)	38(1)
C(20)	938(2)	7652(2)	5706(1)	40(1)
C(21)	537(2)	7611(2)	6397(1)	33(1)
C(22)	-420(2)	9739(2)	7910(1)	26(1)
C(23)	-146(2)	10558(2)	8521(2)	46(1)
C(24)	-720(3)	11570(2)	8485(2)	57(1)
C(25)	-1561(2)	11773(2)	7867(2)	45(1)
C(26)	-1844(2)	10955(2)	7264(2)	44(1)
C(27)	-1261(2)	9945(2)	7287(2)	37(1)

A6.3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for **162**.

Pd(1)-P(1)	2.2344(5)	C(24)-C(25)	1.369(5)
Pd(1)-As(1)	2.3142(2)	C(25)-C(26)	1.386(4)
Pd(1)-Cl(2)	2.3395(5)	C(26)-C(27)	1.392(3)
Pd(1)-Cl(1)	2.3589(5)		
As(1)-C(1)	1.914(2)	P(1)-Pd(1)-As(1)	85.761(14)
As(1)-C(7)	1.921(2)	P(1)-Pd(1)-Cl(2)	93.20(2)
As(1)-C(14)	1.937(2)	As(1)-Pd(1)-Cl(2)	178.575(17)
P(1)-C(15)	1.798(2)	P(1)-Pd(1)-Cl(1)	173.85(2)
P(1)-C(22)	1.815(2)	As(1)-Pd(1)-Cl(1)	88.110(16)
P(1)-C(16)	1.832(2)	Cl(2)-Pd(1)-Cl(1)	92.94(2)
C(1)-C(2)	1.384(3)	C(1)-As(1)-C(7)	103.82(8)
C(1)-C(6)	1.388(3)	C(1)-As(1)-C(14)	105.94(9)
C(2)-C(3)	1.386(3)	C(7)-As(1)-C(14)	106.12(8)
C(3)-C(4)	1.369(5)	C(1)-As(1)-Pd(1)	116.34(7)
C(4)-C(5)	1.383(4)	C(7)-As(1)-Pd(1)	116.32(6)
C(5)-C(6)	1.385(3)	C(14)-As(1)-Pd(1)	107.44(6)
C(7)-C(8)	1.389(3)	C(15)-P(1)-C(22)	105.73(10)
C(7)-C(12)	1.392(3)	C(15)-P(1)-C(16)	102.76(9)
C(8)-C(9)	1.395(3)	C(22)-P(1)-C(16)	104.26(9)
C(9)-C(10)	1.388(4)	C(15)-P(1)-Pd(1)	110.66(7)
C(10)-C(11)	1.366(4)	C(22)-P(1)-Pd(1)	116.86(7)
C(11)-C(12)	1.392(3)	C(16)-P(1)-Pd(1)	115.24(6)
C(13)-C(14)	1.488(3)	C(2)-C(1)-C(6)	120.3(2)
C(14)-C(15)	1.343(3)	C(2)-C(1)-As(1)	119.43(16)
C(16)-C(21)	1.396(3)	C(6)-C(1)-As(1)	120.27(17)
C(16)-C(17)	1.399(3)	C(1)-C(2)-C(3)	119.4(2)
C(17)-C(18)	1.379(3)	C(4)-C(3)-C(2)	120.6(3)
C(18)-C(19)	1.386(3)	C(3)-C(4)-C(5)	120.0(2)
C(19)-C(20)	1.388(3)	C(4)-C(5)-C(6)	120.2(2)
C(20)-C(21)	1.387(3)	C(5)-C(6)-C(1)	119.5(2)
C(22)-C(27)	1.375(3)	C(8)-C(7)-C(12)	120.1(2)
C(22)-C(23)	1.394(3)	C(8)-C(7)-As(1)	118.50(15)
C(23)-C(24)	1.386(4)	C(12)-C(7)-As(1)	121.34(15)

C(7)-C(8)-C(9)	119.7(2)	C(17)-C(18)-C(19)	120.3(2)
C(10)-C(9)-C(8)	119.6(2)	C(18)-C(19)-C(20)	119.8(2)
C(11)-C(10)-C(9)	120.7(2)	C(21)-C(20)-C(19)	120.3(2)
C(10)-C(11)-C(12)	120.5(2)	C(20)-C(21)-C(16)	120.0(2)
C(11)-C(12)-C(7)	119.4(2)	C(27)-C(22)-C(23)	119.4(2)
C(15)-C(14)-C(13)	124.87(18)	C(27)-C(22)-P(1)	119.88(17)
C(15)-C(14)-As(1)	113.98(14)	C(23)-C(22)-P(1)	120.68(18)
C(13)-C(14)-As(1)	121.02(16)	C(24)-C(23)-C(22)	119.4(3)
C(14)-C(15)-P(1)	122.10(15)	C(25)-C(24)-C(23)	121.2(3)
C(21)-C(16)-C(17)	119.14(19)	C(24)-C(25)-C(26)	119.6(2)
C(21)-C(16)-P(1)	121.56(15)	C(25)-C(26)-C(27)	119.6(2)
C(17)-C(16)-P(1)	119.28(15)	C(22)-C(27)-C(26)	120.7(2)
C(18)-C(17)-C(16)	120.41(19)		

Symmetry transformations used to generate equivalent atoms:

A6.4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **162**. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^* 2U^{11} + \dots + 2h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Pd(1)	18(1)	20(1)	19(1)	0(1)	1(1)	-3(1)
As(1)	22(1)	25(1)	19(1)	3(1)	1(1)	-1(1)
P(1)	19(1)	17(1)	20(1)	2(1)	0(1)	-2(1)
Cl(1)	35(1)	31(1)	40(1)	6(1)	3(1)	-14(1)
Cl(2)	24(1)	35(1)	25(1)	-2(1)	-4(1)	-1(1)
C(1)	25(1)	30(1)	26(1)	7(1)	9(1)	4(1)
C(2)	39(1)	38(1)	35(1)	0(1)	12(1)	5(1)
C(3)	48(2)	52(2)	52(2)	-5(1)	23(1)	14(1)
C(4)	49(2)	52(2)	64(2)	19(1)	33(2)	26(1)
C(5)	44(1)	65(2)	47(2)	24(1)	16(1)	27(1)
C(6)	37(1)	51(2)	28(1)	10(1)	7(1)	16(1)
C(7)	21(1)	27(1)	21(1)	3(1)	2(1)	2(1)
C(8)	44(1)	28(1)	33(1)	2(1)	15(1)	1(1)
C(9)	48(1)	36(1)	42(1)	13(1)	23(1)	9(1)
C(10)	44(1)	48(1)	30(1)	8(1)	18(1)	14(1)

C(11)	37(1)	43(1)	30(1)	-7(1)	8(1)	5(1)
C(12)	26(1)	30(1)	29(1)	-2(1)	3(1)	-1(1)
C(13)	26(1)	52(1)	23(1)	4(1)	-3(1)	-9(1)
C(14)	20(1)	32(1)	21(1)	-1(1)	-1(1)	-5(1)
C(15)	24(1)	27(1)	24(1)	0(1)	2(1)	-7(1)
C(16)	24(1)	21(1)	20(1)	2(1)	2(1)	1(1)
C(17)	33(1)	26(1)	27(1)	1(1)	6(1)	-4(1)
C(18)	36(1)	34(1)	33(1)	5(1)	12(1)	-6(1)
C(19)	45(1)	41(1)	32(1)	5(1)	18(1)	5(1)
C(20)	51(1)	40(1)	33(1)	-10(1)	14(1)	-6(1)
C(21)	39(1)	28(1)	33(1)	-6(1)	9(1)	-9(1)
C(22)	29(1)	23(1)	26(1)	5(1)	9(1)	0(1)
C(23)	56(2)	40(1)	37(1)	-14(1)	2(1)	6(1)
C(24)	78(2)	39(1)	57(2)	-18(1)	20(2)	10(1)
C(25)	51(2)	32(1)	62(2)	9(1)	33(1)	12(1)
C(26)	40(1)	40(1)	52(2)	15(1)	12(1)	14(1)
C(27)	36(1)	32(1)	40(1)	1(1)	0(1)	6(1)

A6.5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **162**.

	x	y	z	U(eq)
H(2)	1174	4745	8146	44
H(3)	2242	3120	8184	59
H(4)	3381	2592	9368	62
H(5)	3531	3737	10516	61
H(6)	2492	5386	10486	47
H(8)	-18	4924	10219	40
H(9)	-568	4924	11448	48
H(10)	-335	6578	12254	47
H(11)	390	8227	11838	44
H(12)	901	8265	10599	34
H(13A)	3227	8629	9769	53
H(13B)	3258	7249	9832	53

H(13C)	2707	7988	10420	53
H(15)	1916	9306	8654	30
H(17)	1652	9951	7256	35
H(18)	2323	10003	6097	40
H(19)	1865	8576	5113	45
H(20)	761	7065	5309	49
H(21)	79	7002	6470	40
H(23)	429	10423	8958	55
H(24)	-527	12133	8897	68
H(25)	-1949	12470	7852	54
H(26)	-2434	11084	6838	52
H(27)	-1446	9392	6867	44

A7. X-ray Crystallographic Data for (S_C, R_C)-165**A7.1. Crystal data and structure refinement for (S_C, R_C)-165**

Identification code	leung98a
Empirical formula	C ₄₁ H ₄₂ As Cl N O ₄ P Pd 0.5CH ₂ Cl ₂
Formula weight	902.96
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)
Unit cell dimensions	a = 19.4261(9) Å $\alpha = 90^\circ$. b = 9.7061(4) Å $\beta = 106.477(2)^\circ$. c = 22.1846(10) Å $\gamma = 90^\circ$.
Volume	4011.2(3) Å ³
Z	4
Density (calculated)	1.495 Mg/m ³
Absorption coefficient	1.496 mm ⁻¹
F(000)	1836
Crystal size	0.10 x 0.10 x 0.10 mm ³
Theta range for data collection	2.12 to 30.51°.
Index ranges	-25 ≤ h ≤ 27, -13 ≤ k ≤ 12, -31 ≤ l ≤ 26
Reflections collected	46632
Independent reflections	22643 [R(int) = 0.0582]
Completeness to theta = 30.51°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8648 and 0.8648
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	22643 / 1 / 924
Goodness-of-fit on F ²	0.967
Final R indices [I > 2σ(I)]	R1 = 0.0537, wR2 = 0.1003
R indices (all data)	R1 = 0.1228, wR2 = 0.1239
Absolute structure parameter	-0.012(9)
Largest diff. peak and hole	0.595 and -0.529 e.Å ⁻³

A7.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (S_C, R_C) -**165**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	3736(1)	5359(1)	2471(1)	35(1)
Pd(2)	1088(1)	346(1)	7461(1)	32(1)
As(1)	3514(1)	4649(1)	3475(1)	40(1)
As(2)	1398(1)	-462(1)	6512(1)	38(1)
N(1)	4316(3)	7233(5)	2771(2)	53(2)
N(2)	365(2)	2003(5)	7049(2)	36(1)
P(1)	3127(1)	3410(2)	2108(1)	34(1)
P(2)	1770(1)	-1475(2)	7910(1)	32(1)
Cl(1)	1017(1)	1111(2)	3252(1)	58(1)
Cl(2)	4056(1)	6056(2)	6832(1)	68(1)
Cl(3)	2752(1)	3252(3)	9463(1)	91(1)
Cl(4)	2653(1)	3910(3)	8156(1)	94(1)
O(1)	994(3)	308(7)	3773(3)	105(2)
O(2)	304(3)	1338(9)	2887(4)	142(3)
O(3)	1386(3)	374(7)	2891(2)	102(2)
O(4)	1352(3)	2371(6)	3423(3)	103(2)
O(5)	3994(5)	5255(9)	6293(4)	162(3)
O(6)	3778(4)	5278(7)	7254(3)	124(2)
O(7)	4768(4)	6284(13)	7084(5)	224(5)
O(8)	3728(5)	7273(8)	6692(4)	181(4)
C(1)	3966(3)	5893(6)	1654(3)	37(1)
C(2)	3624(3)	5488(7)	1033(2)	40(1)
C(3)	3833(3)	6021(6)	531(3)	45(2)
C(4)	4395(3)	6965(6)	630(3)	37(1)
C(5)	4622(3)	7511(7)	125(3)	52(2)
C(6)	5158(4)	8458(8)	221(3)	62(2)
C(7)	5508(3)	8903(7)	832(3)	54(2)
C(8)	5303(3)	8403(6)	1332(3)	48(2)
C(9)	4746(3)	7414(6)	1249(3)	39(1)
C(10)	4518(3)	6843(6)	1756(3)	40(1)
C(11)	4894(3)	7211(7)	2433(3)	50(2)
C(12)	5491(3)	6189(8)	2726(3)	73(2)

C(13)	4656(4)	7417(8)	3461(3)	86(3)
C(14)	3831(4)	8453(7)	2525(4)	81(3)
C(15)	4386(3)	4381(6)	4161(3)	47(2)
C(16)	4942(3)	3674(7)	4024(3)	57(2)
C(17)	5587(4)	3458(8)	4486(4)	74(2)
C(18)	5663(4)	3988(9)	5074(4)	76(2)
C(19)	5119(4)	4689(8)	5214(3)	72(2)
C(20)	4476(4)	4887(7)	4762(3)	61(2)
C(21)	2877(2)	5672(4)	3842(2)	48(2)
C(22)	2668(2)	6986(4)	3614(2)	63(2)
C(23)	2231(3)	7772(4)	3879(3)	82(3)
C(24)	2004(2)	7244(6)	4373(3)	89(3)
C(25)	2213(3)	5929(7)	4601(2)	118(4)
C(26)	2649(3)	5143(5)	4335(2)	92(3)
C(27)	3258(4)	1820(7)	3889(3)	69(2)
C(28)	3064(3)	2799(6)	3337(3)	42(2)
C(29)	3240(3)	2193(6)	2756(3)	41(1)
C(30)	2171(3)	3717(6)	1816(3)	36(1)
C(31)	1665(3)	2797(6)	1912(3)	44(2)
C(32)	945(3)	3038(8)	1664(3)	55(2)
C(33)	707(3)	4184(8)	1302(3)	57(2)
C(34)	1193(3)	5122(7)	1198(3)	53(2)
C(35)	1920(3)	4911(6)	1460(3)	45(2)
C(36)	3328(3)	2341(6)	1505(3)	39(1)
C(37)	2817(4)	1633(8)	1072(4)	78(3)
C(38)	3008(4)	712(11)	654(4)	112(4)
C(39)	3700(4)	628(8)	651(4)	79(2)
C(40)	4218(4)	1307(8)	1078(4)	78(3)
C(41)	4038(3)	2156(7)	1508(3)	62(2)
C(42)	824(3)	1009(6)	8243(3)	35(1)
C(43)	1214(3)	847(6)	8885(3)	38(1)
C(44)	997(3)	1492(6)	9353(3)	43(2)
C(45)	376(3)	2323(6)	9207(3)	40(2)
C(46)	137(4)	2942(7)	9700(3)	63(2)
C(47)	-464(4)	3759(7)	9548(4)	67(2)
C(48)	-855(4)	3957(7)	8928(4)	63(2)
C(49)	-639(3)	3389(7)	8445(3)	56(2)
C(50)	-22(3)	2521(6)	8571(3)	41(1)

C(51)	218(3)	1857(6)	8097(3)	35(1)
C(52)	-193(3)	1979(6)	7409(3)	43(2)
C(53)	-714(3)	787(7)	7214(3)	55(2)
C(54)	13(3)	1948(7)	6363(3)	56(2)
C(55)	759(3)	3333(6)	7174(3)	53(2)
C(56)	583(3)	-825(6)	5780(3)	43(2)
C(57)	15(3)	-1557(7)	5885(3)	54(2)
C(58)	-619(4)	-1704(7)	5396(3)	61(2)
C(59)	-666(4)	-1124(8)	4820(3)	63(2)
C(60)	-100(4)	-416(7)	4717(3)	61(2)
C(61)	532(3)	-238(6)	5206(3)	48(2)
C(62)	2063(3)	628(6)	6209(3)	45(2)
C(63)	2340(4)	197(10)	5731(3)	89(3)
C(64)	2803(5)	1026(11)	5524(4)	101(3)
C(65)	3008(4)	2286(10)	5807(4)	85(3)
C(66)	2749(4)	2698(8)	6287(5)	82(3)
C(67)	2288(3)	1860(7)	6497(3)	56(2)
C(68)	1723(4)	-3326(7)	6204(3)	75(2)
C(69)	1871(3)	-2276(6)	6730(3)	42(2)
C(70)	1664(3)	-2793(6)	7300(3)	42(2)
C(71)	2725(3)	-1147(6)	8179(3)	35(1)
C(72)	3224(3)	-2101(7)	8110(3)	47(2)
C(73)	3960(3)	-1842(8)	8339(3)	60(2)
C(74)	4182(3)	-615(8)	8631(3)	64(2)
C(75)	3702(3)	359(9)	8714(3)	64(2)
C(76)	2971(3)	99(6)	8461(3)	49(2)
C(77)	1581(3)	-2403(6)	8562(3)	37(1)
C(78)	2071(3)	-2451(7)	9149(3)	52(2)
C(79)	1901(4)	-3142(8)	9643(3)	68(2)
C(80)	1266(4)	-3832(8)	9532(4)	70(2)
C(81)	785(3)	-3787(7)	8949(4)	62(2)
C(82)	934(3)	-3070(7)	8464(3)	51(2)
C(83)	2205(4)	3932(10)	8751(4)	89(3)

A7.3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for (S_C, R_C)-**165**.

Pd(1)-C(1)	2.051(5)	C(1)-C(10)	1.383(7)
Pd(1)-N(1)	2.144(5)	C(1)-C(2)	1.406(7)
Pd(1)-P(1)	2.2551(16)	C(2)-C(3)	1.388(7)
Pd(1)-As(1)	2.4845(7)	C(3)-C(4)	1.395(8)
Pd(2)-C(42)	2.048(5)	C(4)-C(5)	1.417(7)
Pd(2)-N(2)	2.161(4)	C(4)-C(9)	1.419(8)
Pd(2)-P(2)	2.2632(15)	C(5)-C(6)	1.359(9)
Pd(2)-As(2)	2.4745(7)	C(6)-C(7)	1.401(9)
As(1)-C(21)	1.936(3)	C(7)-C(8)	1.369(8)
As(1)-C(15)	1.948(6)	C(8)-C(9)	1.420(8)
As(1)-C(28)	1.983(6)	C(9)-C(10)	1.432(7)
As(2)-C(62)	1.933(6)	C(10)-C(11)	1.514(8)
As(2)-C(56)	1.952(6)	C(11)-C(12)	1.525(9)
As(2)-C(69)	1.982(6)	C(15)-C(16)	1.385(8)
N(1)-C(13)	1.495(8)	C(15)-C(20)	1.385(8)
N(1)-C(14)	1.516(8)	C(16)-C(17)	1.392(9)
N(1)-C(11)	1.517(7)	C(17)-C(18)	1.372(10)
N(2)-C(54)	1.481(7)	C(18)-C(19)	1.365(10)
N(2)-C(55)	1.486(7)	C(19)-C(20)	1.376(9)
N(2)-C(52)	1.519(6)	C(21)-C(22)	1.3900
P(1)-C(30)	1.809(5)	C(21)-C(26)	1.3900
P(1)-C(36)	1.821(6)	C(22)-C(23)	1.3900
P(1)-C(29)	1.824(5)	C(23)-C(24)	1.3900
P(2)-C(71)	1.807(6)	C(24)-C(25)	1.3900
P(2)-C(77)	1.828(5)	C(25)-C(26)	1.3900
P(2)-C(70)	1.831(6)	C(27)-C(28)	1.511(8)
Cl(1)-O(4)	1.387(5)	C(28)-C(29)	1.541(8)
Cl(1)-O(1)	1.405(5)	C(30)-C(31)	1.390(7)
Cl(1)-O(2)	1.408(6)	C(30)-C(35)	1.409(7)
Cl(1)-O(3)	1.412(5)	C(31)-C(32)	1.369(8)
Cl(2)-O(8)	1.336(7)	C(32)-C(33)	1.373(9)
Cl(2)-O(7)	1.355(8)	C(33)-C(34)	1.377(9)
Cl(2)-O(5)	1.403(7)	C(34)-C(35)	1.381(7)
Cl(2)-O(6)	1.422(6)	C(36)-C(37)	1.357(8)
Cl(3)-C(83)	1.761(8)	C(36)-C(41)	1.389(7)
Cl(4)-C(83)	1.776(7)	C(37)-C(38)	1.411(9)

C(38)-C(39)	1.350(9)	C(78)-C(79)	1.403(8)
C(39)-C(40)	1.342(10)	C(79)-C(80)	1.363(9)
C(40)-C(41)	1.378(9)	C(80)-C(81)	1.364(9)
C(42)-C(51)	1.398(7)	C(81)-C(82)	1.379(8)
C(42)-C(43)	1.420(7)		
C(43)-C(44)	1.377(7)	C(1)-Pd(1)-N(1)	80.4(2)
C(44)-C(45)	1.411(8)	C(1)-Pd(1)-P(1)	96.96(17)
C(45)-C(50)	1.417(8)	N(1)-Pd(1)-P(1)	177.34(14)
C(45)-C(46)	1.436(8)	C(1)-Pd(1)-As(1)	177.15(16)
C(46)-C(47)	1.372(9)	N(1)-Pd(1)-As(1)	99.54(13)
C(47)-C(48)	1.384(10)	P(1)-Pd(1)-As(1)	83.12(4)
C(48)-C(49)	1.371(8)	C(42)-Pd(2)-N(2)	80.5(2)
C(49)-C(50)	1.427(8)	C(42)-Pd(2)-P(2)	97.40(16)
C(50)-C(51)	1.418(7)	N(2)-Pd(2)-P(2)	175.41(13)
C(51)-C(52)	1.514(8)	C(42)-Pd(2)-As(2)	179.52(15)
C(52)-C(53)	1.516(8)	N(2)-Pd(2)-As(2)	99.27(12)
C(56)-C(61)	1.372(7)	P(2)-Pd(2)-As(2)	82.76(4)
C(56)-C(57)	1.387(8)	C(21)-As(1)-C(15)	105.0(2)
C(57)-C(58)	1.398(9)	C(21)-As(1)-C(28)	102.9(2)
C(58)-C(59)	1.376(9)	C(15)-As(1)-C(28)	104.3(2)
C(59)-C(60)	1.370(9)	C(21)-As(1)-Pd(1)	121.92(13)
C(60)-C(61)	1.399(8)	C(15)-As(1)-Pd(1)	113.87(17)
C(62)-C(67)	1.367(8)	C(28)-As(1)-Pd(1)	107.07(17)
C(62)-C(63)	1.384(8)	C(62)-As(2)-C(56)	105.9(2)
C(63)-C(64)	1.379(10)	C(62)-As(2)-C(69)	105.1(3)
C(64)-C(65)	1.381(11)	C(56)-As(2)-C(69)	104.7(3)
C(65)-C(66)	1.361(10)	C(62)-As(2)-Pd(2)	118.05(18)
C(66)-C(67)	1.386(9)	C(56)-As(2)-Pd(2)	115.47(17)
C(68)-C(69)	1.514(8)	C(69)-As(2)-Pd(2)	106.39(17)
C(69)-C(70)	1.517(7)	C(13)-N(1)-C(14)	109.0(5)
C(71)-C(72)	1.380(7)	C(13)-N(1)-C(11)	109.6(5)
C(71)-C(76)	1.383(8)	C(14)-N(1)-C(11)	107.7(5)
C(72)-C(73)	1.397(8)	C(13)-N(1)-Pd(1)	117.4(4)
C(73)-C(74)	1.366(10)	C(14)-N(1)-Pd(1)	109.4(4)
C(74)-C(75)	1.376(9)	C(11)-N(1)-Pd(1)	103.4(3)
C(75)-C(76)	1.393(8)	C(54)-N(2)-C(55)	106.6(5)
C(77)-C(82)	1.376(8)	C(54)-N(2)-C(52)	110.4(5)
C(77)-C(78)	1.378(8)	C(55)-N(2)-C(52)	108.8(4)

C(54)-N(2)-Pd(2)	117.6(3)	C(7)-C(8)-C(9)	121.4(6)
C(55)-N(2)-Pd(2)	109.2(3)	C(4)-C(9)-C(8)	118.2(5)
C(52)-N(2)-Pd(2)	103.9(3)	C(4)-C(9)-C(10)	118.1(5)
C(30)-P(1)-C(36)	104.0(3)	C(8)-C(9)-C(10)	123.7(6)
C(30)-P(1)-C(29)	105.8(3)	C(1)-C(10)-C(9)	121.9(5)
C(36)-P(1)-C(29)	102.0(3)	C(1)-C(10)-C(11)	116.9(5)
C(30)-P(1)-Pd(1)	111.77(19)	C(9)-C(10)-C(11)	121.1(5)
C(36)-P(1)-Pd(1)	122.62(19)	C(10)-C(11)-N(1)	106.1(5)
C(29)-P(1)-Pd(1)	109.2(2)	C(10)-C(11)-C(12)	111.4(5)
C(71)-P(2)-C(77)	104.1(3)	N(1)-C(11)-C(12)	112.2(5)
C(71)-P(2)-C(70)	104.9(3)	C(16)-C(15)-C(20)	119.7(6)
C(77)-P(2)-C(70)	103.6(3)	C(16)-C(15)-As(1)	117.0(5)
C(71)-P(2)-Pd(2)	115.18(19)	C(20)-C(15)-As(1)	123.3(5)
C(77)-P(2)-Pd(2)	120.60(18)	C(15)-C(16)-C(17)	120.5(7)
C(70)-P(2)-Pd(2)	106.92(19)	C(18)-C(17)-C(16)	118.4(7)
O(4)-Cl(1)-O(1)	112.7(4)	C(19)-C(18)-C(17)	121.5(7)
O(4)-Cl(1)-O(2)	109.2(5)	C(18)-C(19)-C(20)	120.4(7)
O(1)-Cl(1)-O(2)	107.7(4)	C(19)-C(20)-C(15)	119.5(7)
O(4)-Cl(1)-O(3)	109.1(4)	C(22)-C(21)-C(26)	120.0
O(1)-Cl(1)-O(3)	109.0(4)	C(22)-C(21)-As(1)	118.2(3)
O(2)-Cl(1)-O(3)	109.1(4)	C(26)-C(21)-As(1)	121.7(3)
O(8)-Cl(2)-O(7)	108.3(7)	C(21)-C(22)-C(23)	120.0
O(8)-Cl(2)-O(5)	111.9(6)	C(24)-C(23)-C(22)	120.0
O(7)-Cl(2)-O(5)	105.8(6)	C(25)-C(24)-C(23)	120.0
O(8)-Cl(2)-O(6)	112.2(4)	C(26)-C(25)-C(24)	120.0
O(7)-Cl(2)-O(6)	110.4(5)	C(25)-C(26)-C(21)	120.0
O(5)-Cl(2)-O(6)	108.1(4)	C(27)-C(28)-C(29)	112.0(5)
C(10)-C(1)-C(2)	118.4(5)	C(27)-C(28)-As(1)	116.6(5)
C(10)-C(1)-Pd(1)	112.2(4)	C(29)-C(28)-As(1)	106.4(4)
C(2)-C(1)-Pd(1)	129.3(4)	C(28)-C(29)-P(1)	114.0(4)
C(3)-C(2)-C(1)	121.2(5)	C(31)-C(30)-C(35)	117.8(5)
C(2)-C(3)-C(4)	120.9(6)	C(31)-C(30)-P(1)	122.5(5)
C(3)-C(4)-C(5)	121.9(6)	C(35)-C(30)-P(1)	119.6(4)
C(3)-C(4)-C(9)	119.5(5)	C(32)-C(31)-C(30)	121.0(6)
C(5)-C(4)-C(9)	118.6(6)	C(31)-C(32)-C(33)	120.7(6)
C(6)-C(5)-C(4)	121.7(6)	C(32)-C(33)-C(34)	120.0(6)
C(5)-C(6)-C(7)	120.0(6)	C(33)-C(34)-C(35)	120.0(6)
C(8)-C(7)-C(6)	120.1(6)	C(34)-C(35)-C(30)	120.5(6)

C(37)-C(36)-C(41)	117.7(6)	C(59)-C(58)-C(57)	119.4(7)
C(37)-C(36)-P(1)	122.8(4)	C(60)-C(59)-C(58)	121.1(7)
C(41)-C(36)-P(1)	119.4(5)	C(59)-C(60)-C(61)	120.0(7)
C(36)-C(37)-C(38)	120.6(6)	C(56)-C(61)-C(60)	119.0(6)
C(39)-C(38)-C(37)	119.3(8)	C(67)-C(62)-C(63)	118.8(6)
C(40)-C(39)-C(38)	121.0(7)	C(67)-C(62)-As(2)	118.2(5)
C(39)-C(40)-C(41)	119.7(7)	C(63)-C(62)-As(2)	123.0(5)
C(40)-C(41)-C(36)	121.3(7)	C(64)-C(63)-C(62)	120.7(8)
C(51)-C(42)-C(43)	118.2(5)	C(63)-C(64)-C(65)	119.9(8)
C(51)-C(42)-Pd(2)	112.8(4)	C(66)-C(65)-C(64)	119.5(8)
C(43)-C(42)-Pd(2)	128.6(4)	C(65)-C(66)-C(67)	120.6(8)
C(44)-C(43)-C(42)	121.1(5)	C(62)-C(67)-C(66)	120.5(7)
C(43)-C(44)-C(45)	120.8(5)	C(68)-C(69)-C(70)	112.5(5)
C(44)-C(45)-C(50)	119.7(5)	C(68)-C(69)-As(2)	115.9(4)
C(44)-C(45)-C(46)	120.3(6)	C(70)-C(69)-As(2)	106.4(4)
C(50)-C(45)-C(46)	120.0(6)	C(69)-C(70)-P(2)	112.6(4)
C(47)-C(46)-C(45)	119.4(7)	C(72)-C(71)-C(76)	118.2(5)
C(46)-C(47)-C(48)	120.9(6)	C(72)-C(71)-P(2)	122.2(5)
C(49)-C(48)-C(47)	121.2(7)	C(76)-C(71)-P(2)	119.7(4)
C(48)-C(49)-C(50)	120.7(7)	C(71)-C(72)-C(73)	121.1(6)
C(45)-C(50)-C(51)	118.4(5)	C(74)-C(73)-C(72)	118.9(6)
C(45)-C(50)-C(49)	117.8(5)	C(73)-C(74)-C(75)	121.8(6)
C(51)-C(50)-C(49)	123.8(6)	C(74)-C(75)-C(76)	118.2(7)
C(42)-C(51)-C(50)	121.9(5)	C(71)-C(76)-C(75)	121.6(6)
C(42)-C(51)-C(52)	116.6(5)	C(82)-C(77)-C(78)	119.2(5)
C(50)-C(51)-C(52)	121.5(5)	C(82)-C(77)-P(2)	119.2(5)
C(51)-C(52)-C(53)	110.3(5)	C(78)-C(77)-P(2)	121.6(4)
C(51)-C(52)-N(2)	106.4(4)	C(77)-C(78)-C(79)	120.2(6)
C(53)-C(52)-N(2)	112.3(5)	C(80)-C(79)-C(78)	119.7(7)
C(61)-C(56)-C(57)	121.2(6)	C(79)-C(80)-C(81)	119.8(7)
C(61)-C(56)-As(2)	121.7(5)	C(80)-C(81)-C(82)	121.1(6)
C(57)-C(56)-As(2)	116.6(5)	C(77)-C(82)-C(81)	119.9(6)
C(56)-C(57)-C(58)	119.2(7)	Cl(3)-C(83)-Cl(4)	111.4(4)

Symmetry transformations used to generate equivalent atoms:

A7.4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (S_C, R_C)-**165**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^* 2U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Pd(1)	41(1)	32(1)	35(1)	-2(1)	17(1)	-5(1)
Pd(2)	38(1)	32(1)	29(1)	2(1)	13(1)	5(1)
As(1)	47(1)	41(1)	35(1)	2(1)	17(1)	0(1)
As(2)	47(1)	39(1)	31(1)	-2(1)	15(1)	3(1)
N(1)	69(4)	51(4)	51(4)	-13(3)	37(3)	-24(3)
N(2)	41(3)	34(3)	34(3)	10(2)	12(2)	13(2)
P(1)	34(1)	31(1)	39(1)	1(1)	14(1)	1(1)
P(2)	34(1)	30(1)	33(1)	3(1)	11(1)	1(1)
Cl(1)	58(1)	51(1)	67(1)	5(1)	21(1)	-6(1)
Cl(2)	74(1)	55(1)	79(2)	2(1)	30(1)	4(1)
Cl(3)	83(2)	98(2)	83(2)	-8(1)	10(1)	-15(1)
Cl(4)	84(2)	92(2)	97(2)	18(1)	13(1)	15(1)
O(1)	152(5)	81(4)	109(5)	36(4)	78(4)	23(5)
O(2)	71(4)	167(7)	156(7)	33(6)	-22(4)	-8(5)
O(3)	166(5)	79(4)	79(4)	-7(4)	67(4)	16(5)
O(4)	116(5)	78(4)	136(6)	-34(4)	71(4)	-41(4)
O(5)	277(10)	107(5)	140(6)	-39(6)	121(7)	-27(7)
O(6)	199(7)	83(4)	116(5)	16(5)	86(5)	-14(5)
O(7)	101(6)	313(14)	231(11)	57(10)	3(6)	-60(8)
O(8)	247(10)	140(7)	214(9)	95(7)	158(8)	116(7)
C(1)	46(3)	29(3)	40(4)	6(3)	19(3)	0(3)
C(2)	37(3)	43(3)	41(3)	8(3)	11(2)	-1(3)
C(3)	45(4)	54(4)	33(3)	5(3)	8(3)	7(3)
C(4)	41(3)	41(3)	33(3)	9(3)	16(3)	10(3)
C(5)	54(4)	67(5)	38(4)	9(3)	17(3)	2(4)
C(6)	57(5)	78(5)	59(5)	24(4)	30(4)	5(4)
C(7)	51(4)	52(4)	68(5)	17(4)	30(4)	2(3)
C(8)	44(4)	49(4)	54(4)	1(3)	20(3)	-8(3)
C(9)	43(4)	29(3)	50(4)	0(3)	22(3)	0(3)
C(10)	51(4)	34(3)	38(4)	-2(3)	19(3)	-3(3)
C(11)	70(5)	49(4)	40(4)	-13(3)	29(3)	-31(3)
C(12)	49(4)	114(7)	47(5)	-5(4)	1(4)	-15(4)
C(13)	131(7)	91(6)	49(5)	-41(4)	47(5)	-75(6)

C(14)	129(7)	24(4)	118(7)	-15(4)	82(6)	-11(4)
C(15)	51(4)	45(4)	47(4)	-2(3)	18(3)	-8(3)
C(16)	47(4)	63(5)	61(5)	-4(4)	14(4)	-3(3)
C(17)	55(5)	76(6)	81(6)	-9(5)	5(4)	-2(4)
C(18)	53(5)	78(6)	82(6)	-2(5)	-4(4)	-12(4)
C(19)	88(6)	74(5)	43(4)	-2(4)	1(4)	-11(5)
C(20)	76(5)	61(5)	44(4)	0(3)	16(4)	-1(4)
C(21)	55(4)	55(5)	39(3)	-8(3)	22(3)	7(3)
C(22)	55(4)	53(5)	79(6)	3(4)	19(4)	8(4)
C(23)	48(5)	67(6)	127(8)	-19(5)	20(5)	13(4)
C(24)	63(5)	116(8)	90(7)	-40(6)	26(5)	12(5)
C(25)	121(8)	187(13)	68(6)	-2(7)	63(6)	39(8)
C(26)	129(7)	92(7)	79(6)	28(5)	70(5)	41(6)
C(27)	82(5)	66(5)	55(5)	27(4)	12(4)	-7(4)
C(28)	41(4)	43(4)	42(4)	17(3)	12(3)	6(3)
C(29)	44(4)	33(3)	44(4)	8(3)	8(3)	0(3)
C(30)	35(3)	40(3)	36(3)	-6(3)	16(3)	0(3)
C(31)	40(4)	45(4)	46(4)	-2(3)	12(3)	-3(3)
C(32)	37(4)	67(5)	59(5)	-11(4)	13(3)	-2(3)
C(33)	36(4)	83(6)	46(4)	-22(4)	4(3)	13(4)
C(34)	51(4)	67(5)	41(4)	4(3)	14(3)	25(4)
C(35)	44(3)	45(4)	53(4)	11(3)	23(3)	11(3)
C(36)	37(3)	37(3)	45(4)	-7(3)	15(3)	-1(3)
C(37)	39(4)	110(7)	81(6)	-39(5)	13(4)	13(4)
C(38)	73(5)	153(10)	102(7)	-80(7)	9(5)	28(6)
C(39)	82(5)	72(6)	93(6)	-37(5)	38(5)	11(5)
C(40)	68(5)	68(5)	117(7)	-25(5)	55(5)	4(4)
C(41)	44(4)	56(5)	91(6)	-24(4)	28(4)	-6(3)
C(42)	37(3)	38(3)	31(3)	-2(3)	10(3)	-2(3)
C(43)	36(3)	45(4)	37(3)	1(3)	16(3)	-5(2)
C(44)	47(4)	52(4)	30(3)	-2(3)	12(3)	-8(3)
C(45)	48(4)	37(3)	39(4)	-10(3)	22(3)	-6(3)
C(46)	83(6)	62(5)	56(5)	-15(4)	40(4)	-11(4)
C(47)	97(6)	50(4)	71(6)	-14(4)	54(5)	3(4)
C(48)	68(5)	49(4)	87(6)	-5(4)	45(5)	15(4)
C(49)	57(4)	56(4)	68(5)	5(4)	35(4)	15(3)
C(50)	44(4)	38(3)	46(4)	0(3)	21(3)	0(3)
C(51)	36(3)	32(3)	40(4)	1(3)	14(3)	1(3)

C(52)	41(4)	49(4)	47(4)	8(3)	23(3)	14(3)
C(53)	48(4)	77(5)	37(4)	5(3)	6(3)	-7(3)
C(54)	65(5)	68(5)	37(4)	20(3)	17(3)	25(4)
C(55)	61(4)	42(4)	62(5)	14(3)	26(4)	8(3)
C(56)	51(4)	43(4)	36(3)	1(3)	14(3)	2(3)
C(57)	55(4)	53(4)	53(4)	5(3)	12(4)	6(3)
C(58)	54(4)	68(5)	56(5)	-17(4)	10(4)	-2(4)
C(59)	60(5)	64(5)	53(5)	-9(4)	-4(4)	11(4)
C(60)	77(5)	58(5)	44(4)	1(4)	12(4)	12(4)
C(61)	59(4)	47(4)	36(4)	-2(3)	11(3)	1(3)
C(62)	51(3)	43(4)	40(3)	-6(3)	13(3)	-6(3)
C(63)	111(6)	93(7)	87(6)	-31(6)	66(5)	-30(6)
C(64)	109(7)	149(10)	67(6)	-4(6)	60(5)	-31(7)
C(65)	64(5)	98(7)	93(7)	23(6)	23(5)	-21(5)
C(66)	61(5)	56(5)	127(8)	10(5)	24(5)	0(4)
C(67)	45(4)	57(5)	68(5)	-3(4)	17(4)	-2(3)
C(68)	88(6)	65(5)	67(5)	-24(4)	16(4)	21(4)
C(69)	44(4)	44(4)	38(4)	-6(3)	12(3)	5(3)
C(70)	51(4)	31(3)	45(4)	1(3)	15(3)	0(3)
C(71)	35(3)	35(3)	38(3)	6(3)	14(3)	4(3)
C(72)	39(4)	48(4)	48(4)	-6(3)	4(3)	1(3)
C(73)	38(4)	69(5)	73(5)	11(4)	16(4)	6(4)
C(74)	43(4)	77(6)	72(5)	12(4)	17(4)	-13(4)
C(75)	60(4)	56(4)	79(5)	-16(5)	25(4)	-21(5)
C(76)	43(3)	41(4)	70(4)	-8(3)	26(3)	-6(3)
C(77)	36(3)	38(3)	39(4)	7(3)	13(3)	5(3)
C(78)	45(4)	64(5)	45(4)	13(3)	12(3)	-8(3)
C(79)	72(5)	89(6)	44(4)	26(4)	19(4)	13(5)
C(80)	63(5)	80(6)	79(6)	29(5)	40(5)	7(4)
C(81)	37(4)	67(5)	88(6)	21(4)	28(4)	0(3)
C(82)	37(4)	57(4)	63(5)	15(3)	21(3)	1(3)
C(83)	78(6)	96(7)	93(7)	17(5)	24(5)	10(5)

A7.5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (S_C, R_C)-**165**.

	x	y	z	U(eq)
H(2)	3252	4851	957	48
H(3)	3594	5745	124	54
H(5)	4399	7214	-282	63
H(6)	5292	8810	-119	74
H(7)	5880	9539	898	65
H(8)	5534	8718	1735	57
H(11)	5101	8135	2447	60
H(12A)	5289	5287	2728	109
H(12B)	5729	6464	3149	109
H(12C)	5830	6172	2485	109
H(13A)	4926	6607	3629	129
H(13B)	4289	7562	3667	129
H(13C)	4970	8200	3530	129
H(14A)	3422	8417	2686	121
H(14B)	3673	8421	2074	121
H(14C)	4090	9293	2658	121
H(16)	4883	3340	3619	68
H(17)	5958	2966	4398	89
H(18)	6095	3867	5385	91
H(19)	5183	5035	5618	87
H(20)	4104	5357	4860	73
H(22)	2820	7340	3283	75
H(23)	2091	8651	3726	98
H(24)	1711	7769	4550	106
H(25)	2060	5576	4931	141
H(26)	2789	4264	4488	110
H(27A)	3022	953	3767	104
H(27B)	3109	2203	4230	104
H(27C)	3769	1680	4020	104
H(28)	2543	2935	3224	50
H(29A)	2933	1403	2609	49
H(29B)	3733	1871	2880	49

H(31)	1817	2007	2150	52
H(32)	615	2420	1741	65
H(33)	218	4327	1127	68
H(34)	1032	5897	953	63
H(35)	2246	5561	1400	55
H(37)	2335	1756	1051	93
H(38)	2660	168	384	135
H(39)	3820	92	348	95
H(40)	4695	1205	1083	94
H(41)	4400	2614	1806	74
H(43)	1623	297	8992	46
H(44)	1263	1377	9771	52
H(46)	387	2791	10119	75
H(47)	-611	4186	9866	80
H(48)	-1271	4484	8836	76
H(49)	-897	3573	8031	68
H(52)	-461	2848	7339	52
H(53A)	-450	-50	7213	83
H(53B)	-1025	954	6799	83
H(53C)	-995	703	7504	83
H(54A)	-321	2698	6245	85
H(54B)	-238	1090	6259	85
H(54C)	370	2022	6141	85
H(55A)	1134	3335	6969	80
H(55B)	966	3445	7618	80
H(55C)	433	4077	7014	80
H(57)	54	-1945	6277	65
H(58)	-1005	-2190	5460	73
H(59)	-1089	-1213	4496	76
H(60)	-135	-53	4321	73
H(61)	912	269	5143	57
H(63)	2213	-662	5547	107
H(64)	2976	738	5195	121
H(65)	3322	2849	5670	102
H(66)	2883	3551	6475	98
H(67)	2130	2137	6837	68
H(68A)	2010	-4132	6344	112
H(68B)	1840	-2938	5847	112

H(68C)	1224	-3574	6087	112
H(69)	2390	-2112	6863	50
H(70A)	1960	-3582	7474	50
H(70B)	1168	-3096	7169	50
H(72)	3068	-2931	7908	56
H(73)	4292	-2493	8294	72
H(74)	4671	-433	8779	77
H(75)	3861	1169	8932	77
H(76)	2642	779	8482	59
H(78)	2515	-2024	9217	62
H(79)	2220	-3129	10045	82
H(80)	1161	-4332	9852	84
H(81)	349	-4247	8878	74
H(82)	597	-3038	8071	61
H(83A)	2075	4872	8819	107
H(83B)	1768	3395	8614	107

A8. X-ray Crystallographic Data for (S_C, R_C, S_P)-172**A8.1. Crystal data and structure refinement for (S_C, R_C, S_P)-172**

Identification code	leung114o	
Empirical formula	C ₃₈ H ₄₂ As Cl N O ₄ P Pd	
Formula weight	824.47	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 12.7487(4) Å	$\alpha = 90^\circ$.
	b = 14.6325(5) Å	$\beta = 90^\circ$.
	c = 19.8038(7) Å	$\gamma = 90^\circ$.
Volume	3694.3(2) Å ³	
Z	4	
Density (calculated)	1.482 Mg/m ³	
Absorption coefficient	1.546 mm ⁻¹	
F(000)	1680	
Crystal size	0.30 x 0.25 x 0.08 mm ³	
Theta range for data collection	1.73 to 30.65°.	
Index ranges	-18 ≤ h ≤ 18, -20 ≤ k ≤ 20, -28 ≤ l ≤ 28	
Reflections collected	80486	
Independent reflections	11376 [R(int) = 0.0498]	
Completeness to theta = 30.65°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8863 and 0.6541	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	11376 / 0 / 429	
Goodness-of-fit on F ²	1.142	
Final R indices [I > 2σ(I)]	R1 = 0.0484, wR2 = 0.1087	
R indices (all data)	R1 = 0.0695, wR2 = 0.1182	
Absolute structure parameter	0.015(12)	
Largest diff. peak and hole	2.450 and -0.988 e.Å ⁻³	

A8.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (S_C, R_C, S_P) -**172**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	7249(1)	1(1)	9557(1)	33(1)
As(1)	8777(1)	-643(1)	10132(1)	35(1)
P(1)	8354(1)	169(1)	8674(1)	42(1)
N(1)	6169(3)	-167(3)	10368(2)	35(1)
C(1)	5920(3)	483(3)	9082(2)	33(1)
C(2)	5715(4)	584(4)	8380(2)	43(1)
C(3)	4738(4)	757(4)	8149(3)	49(1)
C(4)	3879(4)	883(3)	8593(3)	42(1)
C(5)	2843(5)	1098(4)	8366(3)	58(2)
C(6)	2070(5)	1277(5)	8806(4)	69(2)
C(7)	2234(5)	1227(4)	9505(3)	57(1)
C(8)	3204(4)	997(3)	9749(3)	44(1)
C(9)	4056(4)	820(3)	9305(2)	36(1)
C(10)	5095(3)	600(3)	9524(2)	34(1)
C(11)	5340(4)	539(4)	10275(2)	37(1)
C(12)	5692(4)	1497(4)	10525(3)	46(1)
C(13)	5702(4)	-1089(4)	10265(3)	48(1)
C(14)	6583(4)	-141(5)	11072(2)	51(1)
C(15)	9529(3)	277(3)	10645(2)	35(1)
C(16)	9189(4)	1173(4)	10588(3)	45(1)
C(17)	9700(5)	1860(4)	10939(3)	59(2)
C(18)	10551(5)	1644(4)	11345(3)	62(2)
C(19)	10885(5)	758(4)	11399(3)	56(1)
C(20)	10392(4)	69(4)	11046(3)	45(1)
C(21)	8723(4)	-1711(3)	10718(3)	41(1)
C(22)	8768(6)	-1625(4)	11418(3)	60(2)
C(23)	8660(7)	-2401(5)	11817(4)	79(2)
C(24)	8525(6)	-3239(4)	11532(4)	68(2)
C(25)	8459(4)	-3326(4)	10844(3)	51(1)
C(26)	8538(3)	-2554(3)	10435(3)	42(1)
C(27)	10800(4)	-1278(4)	9588(4)	63(2)
C(28)	9717(5)	-976(4)	9388(3)	54(2)

C(29)	9696(4)	-149(5)	8929(3)	57(2)
C(30)	8100(6)	-556(4)	7964(3)	60(2)
C(31)	7350(7)	-1192(4)	7953(3)	72(2)
C(32)	7147(11)	-1786(6)	7396(4)	126(5)
C(33)	8554(4)	1303(4)	8336(2)	39(1)
C(34)	9250(4)	1447(4)	7792(3)	51(1)
C(35)	9450(5)	2327(5)	7558(3)	62(2)
C(36)	8971(5)	3065(4)	7867(3)	56(2)
C(37)	8321(4)	2934(4)	8404(3)	49(1)
C(38)	8101(4)	2057(4)	8640(3)	42(1)
Cl(1)	1850(1)	1087(1)	6387(1)	53(1)
O(1)	1969(4)	720(4)	5727(2)	77(1)
O(2)	1305(4)	1943(3)	6352(3)	75(1)
O(3)	1252(5)	479(4)	6782(3)	95(2)
O(4)	2852(4)	1213(4)	6688(3)	90(2)

A8.3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for (S_C, R_C, S_P)-**172**.

Pd(1)-C(1)	2.062(5)	C(4)-C(9)	1.432(7)
Pd(1)-N(1)	2.131(3)	C(5)-C(6)	1.342(10)
Pd(1)-P(1)	2.2596(12)	C(6)-C(7)	1.401(9)
Pd(1)-As(1)	2.4451(6)	C(7)-C(8)	1.370(7)
As(1)-C(15)	1.940(5)	C(8)-C(9)	1.420(7)
As(1)-C(21)	1.949(5)	C(9)-C(10)	1.430(6)
As(1)-C(28)	1.962(5)	C(10)-C(11)	1.523(6)
P(1)-C(30)	1.790(6)	C(11)-C(12)	1.552(7)
P(1)-C(33)	1.806(5)	C(15)-C(16)	1.386(7)
P(1)-C(29)	1.844(6)	C(15)-C(20)	1.390(6)
N(1)-C(13)	1.488(6)	C(16)-C(17)	1.385(8)
N(1)-C(11)	1.489(6)	C(17)-C(18)	1.388(9)
N(1)-C(14)	1.491(5)	C(18)-C(19)	1.368(9)
C(1)-C(10)	1.379(6)	C(19)-C(20)	1.379(8)
C(1)-C(2)	1.424(6)	C(21)-C(26)	1.376(7)
C(2)-C(3)	1.351(7)	C(21)-C(22)	1.392(8)
C(3)-C(4)	1.417(8)	C(22)-C(23)	1.390(8)
C(4)-C(5)	1.429(8)	C(23)-C(24)	1.360(10)

C(24)-C(25)	1.372(9)	C(13)-N(1)-Pd(1)	105.0(3)
C(25)-C(26)	1.393(8)	C(11)-N(1)-Pd(1)	106.6(2)
C(27)-C(28)	1.503(8)	C(14)-N(1)-Pd(1)	118.2(3)
C(28)-C(29)	1.513(9)	C(10)-C(1)-C(2)	117.9(4)
C(30)-C(31)	1.336(10)	C(10)-C(1)-Pd(1)	112.4(3)
C(31)-C(32)	1.428(10)	C(2)-C(1)-Pd(1)	129.2(4)
C(33)-C(38)	1.383(7)	C(3)-C(2)-C(1)	121.3(5)
C(33)-C(34)	1.412(7)	C(2)-C(3)-C(4)	121.8(5)
C(34)-C(35)	1.391(9)	C(3)-C(4)-C(5)	123.2(5)
C(35)-C(36)	1.384(9)	C(3)-C(4)-C(9)	118.8(4)
C(36)-C(37)	1.362(8)	C(5)-C(4)-C(9)	118.0(5)
C(37)-C(38)	1.395(8)	C(6)-C(5)-C(4)	121.1(5)
Cl(1)-O(3)	1.408(6)	C(5)-C(6)-C(7)	121.5(6)
Cl(1)-O(4)	1.421(5)	C(8)-C(7)-C(6)	119.7(6)
Cl(1)-O(1)	1.422(4)	C(7)-C(8)-C(9)	121.2(5)
Cl(1)-O(2)	1.434(5)	C(8)-C(9)-C(10)	124.2(4)
		C(8)-C(9)-C(4)	118.5(4)
C(1)-Pd(1)-N(1)	81.48(15)	C(10)-C(9)-C(4)	117.3(5)
C(1)-Pd(1)-P(1)	97.02(12)	C(1)-C(10)-C(9)	122.8(4)
N(1)-Pd(1)-P(1)	178.20(10)	C(1)-C(10)-C(11)	117.1(4)
C(1)-Pd(1)-As(1)	177.08(12)	C(9)-C(10)-C(11)	119.9(4)
N(1)-Pd(1)-As(1)	96.85(9)	N(1)-C(11)-C(10)	107.9(4)
P(1)-Pd(1)-As(1)	84.61(4)	N(1)-C(11)-C(12)	112.4(4)
C(15)-As(1)-C(21)	105.2(2)	C(10)-C(11)-C(12)	108.5(4)
C(15)-As(1)-C(28)	105.3(2)	C(16)-C(15)-C(20)	120.1(5)
C(21)-As(1)-C(28)	105.7(2)	C(16)-C(15)-As(1)	117.3(3)
C(15)-As(1)-Pd(1)	111.74(13)	C(20)-C(15)-As(1)	122.6(4)
C(21)-As(1)-Pd(1)	123.97(16)	C(17)-C(16)-C(15)	119.9(5)
C(28)-As(1)-Pd(1)	103.45(16)	C(16)-C(17)-C(18)	119.6(5)
C(30)-P(1)-C(33)	106.2(2)	C(19)-C(18)-C(17)	120.3(6)
C(30)-P(1)-C(29)	103.5(3)	C(18)-C(19)-C(20)	120.8(5)
C(33)-P(1)-C(29)	101.7(3)	C(19)-C(20)-C(15)	119.3(5)
C(30)-P(1)-Pd(1)	115.5(2)	C(26)-C(21)-C(22)	119.7(5)
C(33)-P(1)-Pd(1)	118.33(16)	C(26)-C(21)-As(1)	118.8(4)
C(29)-P(1)-Pd(1)	109.77(18)	C(22)-C(21)-As(1)	121.2(4)
C(13)-N(1)-C(11)	109.2(3)	C(23)-C(22)-C(21)	119.1(6)
C(13)-N(1)-C(14)	107.0(4)	C(24)-C(23)-C(22)	120.9(7)
C(11)-N(1)-C(14)	110.5(4)	C(23)-C(24)-C(25)	120.2(6)

C(24)-C(25)-C(26)	119.9(5)	C(35)-C(34)-C(33)	120.5(5)
C(21)-C(26)-C(25)	120.1(5)	C(36)-C(35)-C(34)	119.6(5)
C(27)-C(28)-C(29)	114.2(5)	C(37)-C(36)-C(35)	120.3(6)
C(27)-C(28)-As(1)	115.8(4)	C(36)-C(37)-C(38)	120.9(6)
C(29)-C(28)-As(1)	104.0(4)	C(33)-C(38)-C(37)	120.3(5)
C(28)-C(29)-P(1)	112.5(4)	O(3)-Cl(1)-O(4)	109.6(4)
C(31)-C(30)-P(1)	123.7(5)	O(3)-Cl(1)-O(1)	109.2(4)
C(30)-C(31)-C(32)	124.5(8)	O(4)-Cl(1)-O(1)	109.8(3)
C(38)-C(33)-C(34)	118.4(5)	O(3)-Cl(1)-O(2)	108.4(3)
C(38)-C(33)-P(1)	120.8(4)	O(4)-Cl(1)-O(2)	110.0(3)
C(34)-C(33)-P(1)	120.6(4)	O(1)-Cl(1)-O(2)	109.7(3)

Symmetry transformations used to generate equivalent atoms:

A8.4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (S_C, R_C, S_P)-**172**. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + \dots + 2h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Pd(1)	39(1)	37(1)	24(1)	3(1)	0(1)	0(1)
As(1)	37(1)	34(1)	33(1)	-1(1)	-2(1)	6(1)
P(1)	49(1)	47(1)	31(1)	4(1)	10(1)	10(1)
N(1)	29(2)	48(2)	27(2)	13(2)	-7(1)	-8(2)
C(1)	39(2)	32(2)	27(2)	-1(2)	0(2)	-7(2)
C(2)	57(3)	46(3)	27(2)	7(2)	-8(2)	-1(2)
C(3)	59(3)	56(3)	31(2)	4(2)	-15(2)	-1(3)
C(4)	54(3)	33(2)	41(2)	11(2)	-19(2)	-12(2)
C(5)	55(3)	60(3)	59(3)	20(3)	-27(3)	-14(3)
C(6)	55(4)	74(4)	79(5)	28(4)	-30(3)	-5(3)
C(7)	42(3)	60(3)	69(4)	18(3)	-7(3)	5(3)
C(8)	43(2)	39(2)	50(3)	10(2)	-8(2)	-2(2)
C(9)	42(2)	26(2)	40(2)	5(2)	-12(2)	-3(2)
C(10)	39(2)	34(2)	30(2)	6(2)	-10(2)	-6(2)
C(11)	35(2)	47(3)	27(2)	3(2)	-5(2)	-2(2)
C(12)	44(3)	54(3)	39(3)	-5(2)	-4(2)	-1(2)
C(13)	36(2)	49(3)	58(3)	13(3)	-1(2)	-5(2)

C(14)	42(2)	84(4)	26(2)	3(3)	-7(2)	1(3)
C(15)	30(2)	39(2)	36(2)	2(2)	-6(2)	8(2)
C(16)	46(3)	42(3)	46(3)	2(2)	-2(2)	9(2)
C(17)	77(4)	35(3)	66(4)	-5(3)	-2(3)	7(3)
C(18)	73(4)	57(4)	56(4)	-12(3)	-3(3)	-17(3)
C(19)	50(3)	65(4)	54(3)	-4(3)	-13(2)	-3(3)
C(20)	39(2)	40(3)	55(3)	0(3)	-9(2)	6(2)
C(21)	43(2)	35(2)	45(3)	5(2)	-5(2)	7(2)
C(22)	88(4)	46(3)	48(3)	11(3)	-16(3)	-8(3)
C(23)	123(7)	62(4)	51(4)	18(3)	-18(4)	-8(4)
C(24)	89(5)	47(3)	68(4)	21(3)	-10(4)	-3(3)
C(25)	42(3)	32(3)	80(4)	-1(3)	9(3)	0(2)
C(26)	34(2)	40(2)	53(3)	-5(2)	3(2)	1(2)
C(27)	44(3)	59(3)	86(4)	6(4)	17(3)	20(3)
C(28)	51(3)	66(4)	45(3)	-3(3)	0(2)	25(3)
C(29)	49(3)	72(4)	49(3)	5(3)	15(2)	19(3)
C(30)	100(5)	42(3)	36(3)	-1(2)	8(3)	5(3)
C(31)	117(6)	50(3)	49(3)	9(3)	-6(4)	1(4)
C(32)	251(14)	61(5)	66(5)	-4(4)	-33(7)	-26(7)
C(33)	34(2)	51(3)	31(2)	4(2)	6(2)	3(2)
C(34)	44(3)	70(4)	38(3)	-2(3)	11(2)	5(3)
C(35)	55(3)	78(4)	52(3)	14(3)	20(3)	-12(3)
C(36)	55(4)	57(3)	56(3)	9(3)	1(3)	-14(3)
C(37)	45(3)	54(3)	47(3)	0(2)	3(2)	-4(2)
C(38)	36(2)	55(3)	35(2)	1(2)	8(2)	5(2)
Cl(1)	47(1)	67(1)	44(1)	-20(1)	-9(1)	13(1)
O(1)	74(3)	101(4)	57(2)	-44(3)	-15(2)	14(3)
O(2)	84(3)	68(3)	73(3)	-20(2)	-7(3)	28(3)
O(3)	110(4)	87(4)	86(4)	9(3)	16(4)	21(4)
O(4)	57(3)	142(5)	72(3)	-58(3)	-23(2)	33(3)

A8.5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (S_C, R_C, S_P)-**172**.

	x	y	z	U(eq)
H(2)	6277	529	8067	52
H(3)	4624	795	7676	58
H(5)	2700	1115	7895	70
H(6)	1396	1440	8640	83
H(7)	1675	1353	9808	69
H(8)	3309	954	10223	53
H(11)	4694	350	10525	44
H(12A)	5727	1498	11019	69
H(12B)	5185	1957	10374	69
H(12C)	6385	1639	10339	69
H(13A)	5216	-1224	10635	71
H(13B)	6262	-1548	10257	71
H(13C)	5323	-1101	9835	71
H(14A)	6000	-61	11389	76
H(14B)	7075	370	11118	76
H(14C)	6946	-716	11171	76
H(16)	8607	1316	10308	54
H(17)	9470	2475	10901	71
H(18)	10904	2113	11588	74
H(19)	11464	616	11682	67
H(20)	10638	-543	11077	54
H(22)	8872	-1043	11620	73
H(23)	8680	-2345	12294	94
H(24)	8477	-3765	11811	82
H(25)	8359	-3911	10646	62
H(26)	8465	-2610	9959	51
H(27A)	11184	-1481	9187	94
H(27B)	10749	-1783	9911	94
H(27C)	11174	-766	9798	94
H(28)	9383	-1493	9137	65
H(29A)	10117	-279	8520	68
H(29B)	10025	374	9166	68

H(30)	8524	-483	7573	71
H(31)	6922	-1255	8343	86
H(32A)	6515	-1581	7158	189
H(32B)	7041	-2410	7561	189
H(32C)	7745	-1774	7085	189
H(34)	9585	940	7584	61
H(35)	9912	2420	7187	74
H(36)	9098	3666	7705	67
H(37)	8012	3447	8621	58
H(38)	7639	1977	9011	50

A9. X-ray Crystallographic Data for ($S_C S_C R_P$)-172**A9.1. Crystal data and structure refinement for ($S_C S_C R_P$)-172**

Identification code	leung125o	
Empirical formula	C ₃₈ H ₄₂ As Cl N O ₄ P Pd	
Formula weight	824.47	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.2977(4) Å	$\alpha = 90^\circ$.
	b = 14.3145(4) Å	$\beta = 90^\circ$.
	c = 25.3270(8) Å	$\gamma = 90^\circ$.
Volume	3733.4(2) Å ³	
Z	4	
Density (calculated)	1.467 Mg/m ³	
Absorption coefficient	1.530 mm ⁻¹	
F(000)	1680	
Crystal size	0.20 x 0.15 x 0.15 mm ³	
Theta range for data collection	1.61 to 30.58°.	
Index ranges	-14 ≤ h ≤ 14, -20 ≤ k ≤ 20, -36 ≤ l ≤ 36	
Reflections collected	48746	
Independent reflections	11363 [R(int) = 0.0444]	
Completeness to theta = 30.58°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8030 and 0.7495	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	11363 / 0 / 429	
Goodness-of-fit on F ²	1.041	
Final R indices [I > 2σ(I)]	R1 = 0.0463, wR2 = 0.1143	
R indices (all data)	R1 = 0.0719, wR2 = 0.1283	
Absolute structure parameter	0.008(12)	
Largest diff. peak and hole	0.989 and -0.549 e.Å ⁻³	

A9.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (S_C, S_C, R_P)-**172**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	26(1)	9072(1)	1177(1)	41(1)
As(1)	2152(1)	9740(1)	1420(1)	44(1)
N(1)	435(3)	7611(2)	1254(1)	43(1)
P(1)	-611(1)	10598(1)	1143(1)	58(1)
C(1)	-1744(4)	8534(3)	977(2)	44(1)
C(2)	-2753(4)	8919(3)	673(2)	48(1)
C(3)	-3865(4)	8454(3)	566(2)	50(1)
C(4)	-4089(4)	7559(3)	769(2)	52(1)
C(5)	-5279(5)	7082(4)	692(3)	65(1)
C(6)	-5498(6)	6226(5)	919(3)	84(2)
C(7)	-4555(7)	5838(5)	1233(3)	90(2)
C(8)	-3363(6)	6236(4)	1301(3)	71(2)
C(9)	-3086(4)	7119(3)	1078(2)	48(1)
C(10)	-1905(4)	7620(3)	1159(2)	44(1)
C(11)	-814(4)	7197(3)	1470(2)	48(1)
C(12)	-930(6)	7385(5)	2055(2)	77(2)
C(13)	674(5)	7219(4)	717(2)	58(1)
C(14)	1574(5)	7343(4)	1582(2)	64(2)
C(15)	3287(4)	9259(3)	1965(2)	48(1)
C(16)	2801(6)	9224(4)	2478(2)	68(1)
C(17)	3539(8)	8856(6)	2881(2)	89(2)
C(18)	4722(8)	8485(6)	2774(3)	97(2)
C(19)	5221(6)	8495(5)	2263(3)	84(2)
C(20)	4494(5)	8885(4)	1855(2)	63(1)
C(21)	3227(5)	9990(3)	808(2)	52(1)
C(22)	4391(5)	10473(4)	836(2)	60(1)
C(23)	5039(7)	10725(4)	377(3)	74(2)
C(24)	4566(7)	10464(5)	-97(3)	84(2)
C(25)	3410(8)	9961(5)	-136(2)	85(2)
C(26)	2755(6)	9721(5)	317(2)	68(1)
C(27)	1696(5)	11012(4)	1669(2)	60(1)
C(28)	2798(6)	11636(4)	1813(2)	62(1)

C(29)	790(6)	11376(4)	1266(3)	77(2)
C(30)	-1794(7)	10915(7)	1615(3)	97(2)
C(31)	-2358(7)	10517(7)	1939(4)	105(3)
C(32)	-3303(8)	10832(7)	2379(3)	106(3)
C(33)	-1168(5)	11111(4)	518(3)	68(2)
C(34)	-965(7)	10680(5)	61(3)	84(2)
C(35)	-1379(11)	11103(6)	-412(3)	112(3)
C(36)	-1968(11)	11896(5)	-415(4)	111(3)
C(37)	-2154(9)	12375(5)	43(4)	108(3)
C(38)	-1769(9)	12002(5)	522(4)	103(3)
Cl(1)	9455(2)	9365(1)	3306(1)	87(1)
O(1)	8780(11)	9882(6)	3684(3)	188(4)
O(2)	9761(9)	9906(6)	2866(3)	164(3)
O(3)	8980(30)	8683(8)	3219(6)	449(17)
O(4)	10505(14)	9190(18)	3559(5)	329(11)

A9.3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for (S_C, S_C, R_P)-**172**.

Pd(1)-C(1)	2.042(4)	C(4)-C(9)	1.440(7)
Pd(1)-N(1)	2.143(3)	C(5)-C(6)	1.372(9)
Pd(1)-P(1)	2.2814(13)	C(6)-C(7)	1.373(11)
Pd(1)-As(1)	2.4672(5)	C(7)-C(8)	1.364(9)
As(1)-C(15)	1.935(5)	C(8)-C(9)	1.415(7)
As(1)-C(21)	1.939(5)	C(9)-C(10)	1.427(6)
As(1)-C(27)	1.983(5)	C(10)-C(11)	1.499(6)
N(1)-C(14)	1.487(6)	C(11)-C(12)	1.512(8)
N(1)-C(13)	1.491(6)	C(15)-C(20)	1.381(7)
N(1)-C(11)	1.517(6)	C(15)-C(16)	1.393(7)
P(1)-C(30)	1.766(7)	C(16)-C(17)	1.378(9)
P(1)-C(33)	1.836(7)	C(17)-C(18)	1.356(11)
P(1)-C(29)	1.849(7)	C(18)-C(19)	1.393(10)
C(1)-C(10)	1.396(6)	C(19)-C(20)	1.393(8)
C(1)-C(2)	1.407(6)	C(21)-C(22)	1.385(7)
C(2)-C(3)	1.351(6)	C(21)-C(26)	1.389(7)
C(3)-C(4)	1.401(7)	C(22)-C(23)	1.387(8)
C(4)-C(5)	1.416(7)	C(23)-C(24)	1.350(10)

C(24)-C(25)	1.394(11)	C(30)-P(1)-Pd(1)	114.8(3)
C(25)-C(26)	1.375(9)	C(33)-P(1)-Pd(1)	120.3(2)
C(27)-C(29)	1.477(8)	C(29)-P(1)-Pd(1)	110.3(2)
C(27)-C(28)	1.489(7)	C(10)-C(1)-C(2)	117.4(4)
C(30)-C(31)	1.156(10)	C(10)-C(1)-Pd(1)	112.2(3)
C(31)-C(32)	1.546(11)	C(2)-C(1)-Pd(1)	130.3(3)
C(33)-C(34)	1.328(9)	C(3)-C(2)-C(1)	122.9(4)
C(33)-C(38)	1.418(9)	C(2)-C(3)-C(4)	121.1(4)
C(34)-C(35)	1.409(10)	C(3)-C(4)-C(5)	122.2(5)
C(35)-C(36)	1.287(11)	C(3)-C(4)-C(9)	118.8(4)
C(36)-C(37)	1.360(12)	C(5)-C(4)-C(9)	119.0(5)
C(37)-C(38)	1.384(12)	C(6)-C(5)-C(4)	120.9(6)
Cl(1)-O(3)	1.113(12)	C(5)-C(6)-C(7)	119.2(6)
Cl(1)-O(4)	1.282(14)	C(8)-C(7)-C(6)	122.8(6)
Cl(1)-O(2)	1.393(6)	C(7)-C(8)-C(9)	120.2(6)
Cl(1)-O(1)	1.397(7)	C(8)-C(9)-C(10)	124.3(5)
		C(8)-C(9)-C(4)	117.6(5)
C(1)-Pd(1)-N(1)	80.18(15)	C(10)-C(9)-C(4)	118.0(4)
C(1)-Pd(1)-P(1)	95.49(12)	C(1)-C(10)-C(9)	121.7(4)
N(1)-Pd(1)-P(1)	173.85(10)	C(1)-C(10)-C(11)	117.5(4)
C(1)-Pd(1)-As(1)	179.34(12)	C(9)-C(10)-C(11)	120.8(4)
N(1)-Pd(1)-As(1)	100.43(9)	C(10)-C(11)-C(12)	112.5(4)
P(1)-Pd(1)-As(1)	83.87(4)	C(10)-C(11)-N(1)	106.8(3)
C(15)-As(1)-C(21)	106.9(2)	C(12)-C(11)-N(1)	110.5(4)
C(15)-As(1)-C(27)	104.1(2)	C(20)-C(15)-C(16)	119.8(5)
C(21)-As(1)-C(27)	102.7(2)	C(20)-C(15)-As(1)	122.6(4)
C(15)-As(1)-Pd(1)	125.19(14)	C(16)-C(15)-As(1)	117.4(4)
C(21)-As(1)-Pd(1)	112.24(15)	C(17)-C(16)-C(15)	120.5(6)
C(27)-As(1)-Pd(1)	103.03(14)	C(18)-C(17)-C(16)	119.8(6)
C(14)-N(1)-C(13)	106.4(4)	C(17)-C(18)-C(19)	120.8(6)
C(14)-N(1)-C(11)	111.5(4)	C(20)-C(19)-C(18)	119.7(6)
C(13)-N(1)-C(11)	108.8(4)	C(15)-C(20)-C(19)	119.4(5)
C(14)-N(1)-Pd(1)	117.3(3)	C(22)-C(21)-C(26)	119.2(5)
C(13)-N(1)-Pd(1)	108.4(3)	C(22)-C(21)-As(1)	123.0(4)
C(11)-N(1)-Pd(1)	104.3(2)	C(26)-C(21)-As(1)	117.7(4)
C(30)-P(1)-C(33)	105.3(3)	C(21)-C(22)-C(23)	120.2(6)
C(30)-P(1)-C(29)	105.6(4)	C(24)-C(23)-C(22)	120.0(6)
C(33)-P(1)-C(29)	98.5(3)	C(23)-C(24)-C(25)	121.0(6)

C(26)-C(25)-C(24)	119.3(7)	C(33)-C(34)-C(35)	119.6(7)
C(25)-C(26)-C(21)	120.4(6)	C(36)-C(35)-C(34)	121.8(9)
C(29)-C(27)-C(28)	116.1(5)	C(35)-C(36)-C(37)	120.4(8)
C(29)-C(27)-As(1)	104.7(4)	C(36)-C(37)-C(38)	120.8(7)
C(28)-C(27)-As(1)	116.6(3)	C(37)-C(38)-C(33)	117.8(8)
C(27)-C(29)-P(1)	113.4(4)	O(3)-Cl(1)-O(4)	107.3(16)
C(31)-C(30)-P(1)	134.4(8)	O(3)-Cl(1)-O(2)	115.5(9)
C(30)-C(31)-C(32)	133.1(10)	O(4)-Cl(1)-O(2)	108.5(9)
C(34)-C(33)-C(38)	119.4(7)	O(3)-Cl(1)-O(1)	112.4(13)
C(34)-C(33)-P(1)	121.1(5)	O(4)-Cl(1)-O(1)	100.4(8)
C(38)-C(33)-P(1)	119.4(6)	O(2)-Cl(1)-O(1)	111.4(5)

Symmetry transformations used to generate equivalent atoms:

A9.4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (S_C, S_C, R_P)-**172**. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Pd(1)	39(1)	38(1)	46(1)	1(1)	-3(1)	2(1)
As(1)	39(1)	42(1)	51(1)	-4(1)	-2(1)	1(1)
N(1)	45(2)	36(2)	47(2)	2(2)	-7(1)	6(1)
P(1)	50(1)	43(1)	82(1)	-6(1)	-12(1)	8(1)
C(1)	47(2)	33(2)	50(2)	-1(2)	-4(2)	2(2)
C(2)	47(2)	41(2)	56(2)	1(2)	-2(2)	3(2)
C(3)	43(2)	47(3)	61(3)	-5(2)	-2(2)	5(2)
C(4)	42(2)	50(3)	63(3)	-16(2)	5(2)	-4(2)
C(5)	48(3)	64(3)	83(4)	-15(3)	6(2)	-8(2)
C(6)	58(3)	65(4)	129(6)	-8(4)	11(4)	-18(3)
C(7)	76(4)	66(4)	127(6)	4(4)	14(4)	-22(3)
C(8)	65(3)	49(3)	98(5)	8(3)	8(3)	-6(2)
C(9)	48(2)	39(2)	58(3)	-1(2)	10(2)	0(2)
C(10)	45(2)	41(2)	46(2)	1(2)	2(2)	-1(2)
C(11)	52(2)	43(2)	50(2)	5(2)	4(2)	2(2)
C(12)	78(4)	97(5)	57(3)	20(3)	6(3)	3(4)

C(13)	55(3)	52(3)	66(3)	-9(2)	6(2)	8(2)
C(14)	51(3)	49(3)	91(4)	1(3)	-19(3)	9(2)
C(15)	46(2)	47(3)	52(2)	-12(2)	-5(2)	6(2)
C(16)	68(3)	74(4)	61(3)	-6(3)	3(3)	15(3)
C(17)	118(5)	100(5)	50(3)	0(3)	-14(3)	23(5)
C(18)	107(6)	97(5)	86(5)	-2(4)	-41(4)	35(5)
C(19)	64(4)	92(5)	97(5)	1(4)	-14(3)	34(3)
C(20)	57(3)	68(3)	65(3)	-9(3)	-7(2)	16(3)
C(21)	52(2)	49(3)	54(3)	0(2)	-2(2)	2(2)
C(22)	49(2)	57(3)	74(3)	-7(3)	4(2)	0(2)
C(23)	63(3)	63(3)	95(4)	14(3)	19(4)	5(3)
C(24)	86(4)	82(5)	85(5)	27(4)	24(4)	16(4)
C(25)	103(5)	97(5)	56(3)	11(3)	-4(3)	21(4)
C(26)	61(3)	84(4)	58(3)	0(3)	-5(2)	1(3)
C(27)	48(2)	50(3)	83(3)	-25(3)	0(2)	3(2)
C(28)	68(3)	56(3)	64(3)	-19(2)	3(3)	-3(3)
C(29)	76(4)	48(3)	108(5)	-5(3)	-12(4)	2(3)
C(30)	82(4)	104(6)	105(5)	24(5)	19(4)	46(4)
C(31)	65(4)	123(7)	127(7)	26(6)	5(4)	0(4)
C(32)	88(5)	132(7)	98(5)	-23(5)	7(4)	-9(5)
C(33)	58(3)	40(3)	106(5)	8(3)	-14(3)	-6(2)
C(34)	99(5)	64(4)	88(4)	7(3)	9(4)	24(4)
C(35)	166(8)	78(5)	92(5)	27(4)	11(5)	28(6)
C(36)	160(9)	63(4)	110(6)	37(4)	5(6)	15(5)
C(37)	122(6)	48(3)	155(8)	34(4)	-35(6)	3(4)
C(38)	126(7)	58(4)	126(6)	-2(4)	-33(5)	15(4)
CI(1)	134(2)	56(1)	71(1)	1(1)	1(1)	-11(1)
O(1)	283(13)	145(6)	137(6)	4(5)	81(8)	57(7)
O(2)	172(7)	177(7)	144(5)	79(5)	53(5)	41(6)
O(3)	930(50)	130(7)	284(16)	-26(9)	90(20)	-263(18)
O(4)	211(12)	620(30)	153(8)	34(14)	31(9)	156(16)

A9.5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (S_C, S_C, R_P)-**172**.

	x	y	z	U(eq)
H(2)	-2652	9520	540	58
H(3)	-4491	8734	354	60
H(5)	-5922	7353	484	78
H(6)	-6275	5912	860	101
H(7)	-4736	5281	1407	108
H(8)	-2730	5925	1496	85
H(11)	-807	6521	1411	58
H(12A)	-860	8044	2119	116
H(12B)	-248	7064	2239	116
H(12C)	-1756	7166	2179	116
H(13A)	1397	7536	558	87
H(13B)	-85	7305	503	87
H(13C)	865	6565	745	87
H(14A)	1565	6680	1640	96
H(14B)	1533	7661	1915	96
H(14C)	2359	7514	1402	96
H(16)	1973	9450	2548	81
H(17)	3227	8862	3225	107
H(18)	5206	8220	3045	116
H(19)	6036	8244	2194	101
H(20)	4817	8893	1512	76
H(22)	4740	10628	1163	72
H(23)	5800	11074	397	88
H(24)	5018	10621	-403	101
H(25)	3086	9790	-465	102
H(26)	1991	9376	295	81
H(27)	1184	10928	1992	72
H(28A)	3340	11732	1509	94
H(28B)	3298	11351	2090	94
H(28C)	2466	12226	1933	94
H(29A)	1259	11466	938	93
H(29B)	471	11981	1380	93

H(30)	-2014	11545	1599	116
H(31)	-2213	9875	1935	126
H(32A)	-3263	11499	2415	159
H(32B)	-3061	10544	2706	159
H(32C)	-4172	10650	2287	159
H(34)	-551	10103	53	100
H(35)	-1223	10801	-731	134
H(36)	-2268	12143	-732	133
H(37)	-2546	12960	33	130
H(38)	-1899	12326	836	124

A10. X-ray Crystallographic Data for (S_C, S_C, R_P)-176**A10.1. Crystal data and structure refinement for (S_C, S_C, R_P)-176**

Identification code	leung182
Empirical formula	C ₃₈ H ₄₂ As Cl N O ₄ P Pd · CH ₂ Cl ₂
Formula weight	909.39
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)
Unit cell dimensions	a = 9.4221(3) Å $\alpha = 90^\circ$. b = 9.7873(3) Å $\beta = 93.025(2)^\circ$. c = 21.1007(6) Å $\gamma = 90^\circ$.
Volume	1943.13(10) Å ³
Z	2
Density (calculated)	1.554 Mg/m ³
Absorption coefficient	1.611 mm ⁻¹
F(000)	924
Crystal size	0.20 x 0.10 x 0.10 mm ³
Theta range for data collection	0.97 to 30.50°.
Index ranges	-13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -30 ≤ l ≤ 30
Reflections collected	22619
Independent reflections	9750 [R(int) = 0.0416]
Completeness to theta = 30.50°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8555 and 0.7389
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	9750 / 1 / 456
Goodness-of-fit on F ²	1.028
Final R indices [I > 2σ(I)]	R1 = 0.0493, wR2 = 0.1248
R indices (all data)	R1 = 0.0618, wR2 = 0.1355
Absolute structure parameter	-0.007(11)
Largest diff. peak and hole	2.031 and -1.661 e.Å ⁻³

A10.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (S_C, S_G, R_P) -**176**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	6195(1)	3226(1)	7457(1)	21(1)
As(1)	7244(1)	4030(1)	6481(1)	24(1)
N(1)	4371(4)	2173(5)	7053(2)	23(1)
P(1)	7985(1)	4398(1)	7960(1)	23(1)
C(1)	5383(5)	2477(5)	8274(2)	21(1)
C(2)	5670(5)	2901(5)	8914(2)	26(1)
C(3)	5002(5)	2287(6)	9402(2)	27(1)
C(4)	3977(5)	1251(6)	9289(2)	26(1)
C(5)	3250(6)	624(6)	9788(2)	31(1)
C(6)	2281(6)	-380(7)	9665(3)	32(1)
C(7)	1992(5)	-847(6)	9037(2)	28(1)
C(8)	2671(5)	-277(6)	8543(2)	26(1)
C(9)	3688(5)	787(5)	8647(2)	22(1)
C(10)	4424(5)	1431(5)	8152(2)	22(1)
C(11)	4236(5)	928(6)	7471(2)	25(1)
C(12)	5361(6)	-150(6)	7346(3)	31(1)
C(13)	3099(5)	3064(7)	7114(2)	31(1)
C(14)	4385(6)	1732(7)	6384(2)	31(1)
C(15)	8658(5)	2854(6)	6137(2)	28(1)
C(16)	8728(6)	1465(7)	6319(3)	36(1)
C(17)	9765(7)	601(9)	6086(4)	49(2)
C(18)	10701(7)	1101(9)	5678(4)	53(2)
C(19)	10656(7)	2448(10)	5493(3)	50(2)
C(20)	9639(6)	3354(9)	5720(3)	42(2)
C(21)	5988(5)	4515(6)	5756(2)	28(1)
C(22)	6147(6)	3894(7)	5162(2)	31(1)
C(23)	5063(7)	4049(8)	4694(3)	38(1)
C(24)	3874(7)	4782(9)	4807(3)	44(2)
C(25)	3723(6)	5419(7)	5387(3)	39(1)
C(26)	4804(6)	5272(7)	5871(3)	35(1)
C(27)	7535(7)	6896(7)	6840(3)	38(1)
C(28)	8418(6)	5605(6)	6753(3)	29(1)

C(29)	9201(5)	5100(6)	7378(2)	27(1)
C(30)	9145(5)	3543(6)	8546(3)	30(1)
C(31)	9645(7)	2291(7)	8519(3)	37(1)
C(32)	9323(10)	1252(9)	8035(4)	60(2)
C(33)	7410(5)	5922(6)	8383(3)	27(1)
C(34)	5972(5)	6257(6)	8393(2)	28(1)
C(35)	5553(6)	7449(6)	8680(3)	32(1)
C(36)	6573(6)	8336(7)	8966(3)	33(1)
C(37)	7990(6)	7993(6)	8962(3)	36(1)
C(38)	8415(6)	6788(7)	8677(3)	33(1)
C(39)	7373(8)	17(12)	593(5)	68(3)
Cl(1)	2178(2)	7400(2)	6832(1)	43(1)
Cl(2)	8624(2)	764(2)	132(1)	56(1)
Cl(3)	7614(2)	445(2)	1410(1)	55(1)
O(1)	2703(7)	8371(8)	6422(3)	76(2)
O(2)	1653(6)	6188(8)	6539(3)	78(2)
O(3)	3412(7)	6943(9)	7234(3)	87(2)
O(4)	1148(5)	8009(7)	7223(3)	63(2)

A10.3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for (S_C, S_C, R_P) -**176**.

Pd(1)-C(1)	2.057(4)	C(2)-C(3)	1.372(7)
Pd(1)-N(1)	2.141(4)	C(3)-C(4)	1.412(8)
Pd(1)-P(1)	2.2576(13)	C(4)-C(5)	1.424(7)
Pd(1)-As(1)	2.4596(6)	C(4)-C(9)	1.442(7)
As(1)-C(15)	1.931(5)	C(5)-C(6)	1.357(9)
As(1)-C(21)	1.944(5)	C(6)-C(7)	1.414(8)
As(1)-C(28)	1.965(6)	C(7)-C(8)	1.370(7)
N(1)-C(14)	1.477(6)	C(8)-C(9)	1.425(7)
N(1)-C(13)	1.493(7)	C(9)-C(10)	1.429(7)
N(1)-C(11)	1.513(7)	C(10)-C(11)	1.521(6)
P(1)-C(30)	1.812(5)	C(11)-C(12)	1.528(8)
P(1)-C(33)	1.834(6)	C(15)-C(20)	1.399(8)
P(1)-C(29)	1.854(5)	C(15)-C(16)	1.413(9)
C(1)-C(10)	1.381(7)	C(16)-C(17)	1.401(9)
C(1)-C(2)	1.426(6)	C(17)-C(18)	1.357(12)

C(18)-C(19)	1.375(13)	C(14)-N(1)-C(11)	109.0(4)
C(19)-C(20)	1.408(10)	C(13)-N(1)-C(11)	109.1(4)
C(21)-C(26)	1.372(8)	C(14)-N(1)-Pd(1)	118.3(3)
C(21)-C(22)	1.407(7)	C(13)-N(1)-Pd(1)	108.4(3)
C(22)-C(23)	1.390(8)	C(11)-N(1)-Pd(1)	104.3(3)
C(23)-C(24)	1.362(10)	C(30)-P(1)-C(33)	103.1(3)
C(24)-C(25)	1.388(10)	C(30)-P(1)-C(29)	104.6(2)
C(25)-C(26)	1.411(8)	C(33)-P(1)-C(29)	103.3(3)
C(27)-C(28)	1.529(9)	C(30)-P(1)-Pd(1)	119.66(19)
C(28)-C(29)	1.557(8)	C(33)-P(1)-Pd(1)	114.15(17)
C(30)-C(31)	1.315(9)	C(29)-P(1)-Pd(1)	110.46(17)
C(31)-C(32)	1.461(10)	C(10)-C(1)-C(2)	118.8(4)
C(33)-C(38)	1.393(8)	C(10)-C(1)-Pd(1)	112.2(3)
C(33)-C(34)	1.395(7)	C(2)-C(1)-Pd(1)	129.1(4)
C(34)-C(35)	1.382(8)	C(3)-C(2)-C(1)	120.7(5)
C(35)-C(36)	1.407(8)	C(2)-C(3)-C(4)	121.7(5)
C(36)-C(37)	1.377(8)	C(3)-C(4)-C(5)	122.5(5)
C(37)-C(38)	1.392(8)	C(3)-C(4)-C(9)	118.5(4)
C(39)-Cl(2)	1.729(9)	C(5)-C(4)-C(9)	119.0(5)
C(39)-Cl(3)	1.777(10)	C(6)-C(5)-C(4)	121.1(5)
Cl(1)-O(1)	1.395(6)	C(5)-C(6)-C(7)	120.5(5)
Cl(1)-O(2)	1.414(7)	C(8)-C(7)-C(6)	120.4(5)
Cl(1)-O(4)	1.435(5)	C(7)-C(8)-C(9)	121.2(5)
Cl(1)-O(3)	1.472(7)	C(8)-C(9)-C(10)	124.0(4)
		C(8)-C(9)-C(4)	117.8(4)
C(1)-Pd(1)-N(1)	80.54(17)	C(10)-C(9)-C(4)	118.2(5)
C(1)-Pd(1)-P(1)	95.12(14)	C(1)-C(10)-C(9)	122.0(4)
N(1)-Pd(1)-P(1)	174.45(11)	C(1)-C(10)-C(11)	117.2(4)
C(1)-Pd(1)-As(1)	177.27(14)	C(9)-C(10)-C(11)	120.7(4)
N(1)-Pd(1)-As(1)	99.82(10)	N(1)-C(11)-C(10)	106.3(4)
P(1)-Pd(1)-As(1)	84.67(4)	N(1)-C(11)-C(12)	112.1(4)
C(15)-As(1)-C(21)	104.6(2)	C(10)-C(11)-C(12)	109.8(4)
C(15)-As(1)-C(28)	100.9(2)	C(20)-C(15)-C(16)	119.0(6)
C(21)-As(1)-C(28)	110.4(2)	C(20)-C(15)-As(1)	121.4(5)
C(15)-As(1)-Pd(1)	116.12(16)	C(16)-C(15)-As(1)	119.6(4)
C(21)-As(1)-Pd(1)	118.85(15)	C(17)-C(16)-C(15)	120.6(6)
C(28)-As(1)-Pd(1)	104.57(15)	C(18)-C(17)-C(16)	119.6(8)
C(14)-N(1)-C(13)	107.5(4)	C(17)-C(18)-C(19)	121.0(7)

C(18)-C(19)-C(20)	121.2(7)	C(38)-C(33)-C(34)	119.2(5)
C(15)-C(20)-C(19)	118.6(8)	C(38)-C(33)-P(1)	120.1(4)
C(26)-C(21)-C(22)	121.1(5)	C(34)-C(33)-P(1)	120.7(4)
C(26)-C(21)-As(1)	117.3(4)	C(35)-C(34)-C(33)	120.4(5)
C(22)-C(21)-As(1)	120.5(4)	C(34)-C(35)-C(36)	120.3(5)
C(23)-C(22)-C(21)	118.5(5)	C(37)-C(36)-C(35)	119.2(6)
C(24)-C(23)-C(22)	120.9(6)	C(36)-C(37)-C(38)	120.7(5)
C(23)-C(24)-C(25)	120.9(5)	C(37)-C(38)-C(33)	120.3(5)
C(24)-C(25)-C(26)	119.3(6)	Cl(2)-C(39)-Cl(3)	113.0(5)
C(21)-C(26)-C(25)	119.3(6)	O(1)-Cl(1)-O(2)	115.3(5)
C(27)-C(28)-C(29)	113.4(5)	O(1)-Cl(1)-O(4)	110.3(5)
C(27)-C(28)-As(1)	112.4(4)	O(2)-Cl(1)-O(4)	111.6(4)
C(29)-C(28)-As(1)	103.4(4)	O(1)-Cl(1)-O(3)	105.7(4)
C(28)-C(29)-P(1)	113.4(3)	O(2)-Cl(1)-O(3)	104.1(5)
C(31)-C(30)-P(1)	127.2(5)	O(4)-Cl(1)-O(3)	109.4(4)
C(30)-C(31)-C(32)	128.1(6)		

Symmetry transformations used to generate equivalent atoms:

A10.4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (S_C, S_C, R_P)-**176**. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Pd(1)	22(1)	27(1)	14(1)	0(1)	0(1)	-3(1)
As(1)	25(1)	30(1)	16(1)	2(1)	2(1)	-1(1)
N(1)	25(2)	31(2)	14(2)	2(2)	-1(1)	-5(2)
P(1)	21(1)	28(1)	20(1)	-1(1)	0(1)	-2(1)
C(1)	25(2)	25(2)	13(2)	2(2)	-2(2)	-1(2)
C(2)	29(2)	30(3)	19(2)	0(2)	-1(2)	-3(2)
C(3)	34(2)	34(3)	14(2)	-1(2)	-2(2)	-3(2)
C(4)	26(2)	31(3)	19(2)	5(2)	3(2)	4(2)
C(5)	38(3)	38(3)	17(2)	3(2)	5(2)	0(2)
C(6)	36(3)	36(3)	24(2)	3(2)	9(2)	-1(2)
C(7)	28(2)	27(2)	28(2)	2(2)	4(2)	-4(2)
C(8)	27(2)	29(3)	22(2)	2(2)	2(2)	0(2)

C(9)	24(2)	26(2)	17(2)	0(2)	2(2)	5(2)
C(10)	23(2)	27(2)	15(2)	2(2)	-1(2)	1(2)
C(11)	29(2)	29(3)	16(2)	-3(2)	-1(2)	-4(2)
C(12)	41(3)	31(3)	21(2)	-1(2)	2(2)	5(2)
C(13)	26(2)	41(3)	25(2)	2(2)	-5(2)	-1(2)
C(14)	36(3)	44(3)	12(2)	-1(2)	-1(2)	-4(2)
C(15)	26(2)	40(3)	19(2)	0(2)	-2(2)	4(2)
C(16)	34(3)	40(3)	34(3)	-3(2)	-6(2)	3(2)
C(17)	40(3)	53(4)	52(4)	-17(3)	-12(3)	3(3)
C(18)	37(3)	70(5)	51(4)	-30(4)	-8(3)	19(3)
C(19)	37(3)	83(6)	30(3)	-9(3)	8(2)	11(4)
C(20)	34(3)	63(4)	30(3)	6(3)	7(2)	9(3)
C(21)	30(2)	37(3)	16(2)	8(2)	-1(2)	-3(2)
C(22)	35(3)	40(3)	19(2)	4(2)	1(2)	1(2)
C(23)	50(3)	43(3)	19(2)	4(2)	-2(2)	-6(3)
C(24)	37(3)	66(5)	30(3)	17(3)	-6(2)	4(3)
C(25)	33(3)	46(4)	37(3)	16(3)	2(2)	11(3)
C(26)	40(3)	38(3)	26(3)	7(2)	3(2)	3(2)
C(27)	47(3)	32(3)	33(3)	1(2)	-2(2)	-6(3)
C(28)	29(2)	36(3)	24(2)	4(2)	5(2)	-3(2)
C(29)	24(2)	36(3)	23(2)	-2(2)	3(2)	-5(2)
C(30)	26(2)	35(3)	27(2)	0(2)	-6(2)	-2(2)
C(31)	37(3)	42(3)	32(3)	1(3)	-8(2)	-3(3)
C(32)	77(5)	48(4)	53(5)	-13(4)	-29(4)	19(4)
C(33)	27(2)	30(3)	26(2)	-2(2)	5(2)	-3(2)
C(34)	28(2)	32(3)	23(2)	3(2)	0(2)	-3(2)
C(35)	27(2)	36(3)	32(3)	6(2)	4(2)	6(2)
C(36)	43(3)	26(3)	32(2)	-1(2)	6(2)	3(2)
C(37)	38(3)	33(3)	35(3)	-9(2)	-3(2)	-6(2)
C(38)	26(2)	39(3)	32(3)	-8(2)	1(2)	0(2)
C(39)	45(4)	82(7)	76(6)	-5(5)	1(4)	-20(4)
Cl(1)	43(1)	42(1)	45(1)	-8(1)	14(1)	-13(1)
Cl(2)	66(1)	58(1)	43(1)	-10(1)	1(1)	-7(1)
Cl(3)	35(1)	70(1)	59(1)	18(1)	9(1)	9(1)
O(1)	87(4)	68(5)	76(4)	21(4)	27(3)	-12(4)
O(2)	59(3)	83(5)	94(5)	-40(4)	34(3)	-24(3)
O(3)	86(4)	98(6)	74(5)	15(4)	-24(4)	9(4)
O(4)	54(3)	74(5)	62(3)	-28(3)	18(2)	0(3)

A10.5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (S_C, S_C, R_P)-**176**.

	x	y	z	U(eq)
H(2)	6330	3617	9005	31
H(3)	5236	2565	9826	33
H(5)	3446	913	10213	37
H(6)	1793	-772	10003	39
H(7)	1323	-1561	8957	33
H(8)	2458	-597	8123	31
H(11)	3267	522	7398	30
H(12A)	5147	-572	6931	47
H(12B)	5357	-852	7677	47
H(12C)	6299	283	7351	47
H(13A)	3162	3854	6831	47
H(13B)	3063	3380	7554	47
H(13C)	2236	2543	6997	47
H(14A)	3653	1033	6302	46
H(14B)	5319	1352	6302	46
H(14C)	4190	2518	6106	46
H(16)	8066	1114	6602	44
H(17)	9812	-330	6214	59
H(18)	11398	512	5518	64
H(19)	11324	2773	5206	60
H(20)	9620	4285	5592	51
H(22)	6974	3381	5083	38
H(23)	5154	3638	4291	45
H(24)	3138	4858	4484	53
H(25)	2900	5948	5458	46
H(26)	4713	5693	6272	42
H(27A)	6674	6663	7058	57
H(27B)	7269	7290	6424	57
H(27C)	8095	7561	7094	57

H(28)	9133	5785	6430	35
H(29A)	9739	5871	7576	33
H(29B)	9893	4384	7273	33
H(30)	9423	4056	8914	35
H(31)	10297	2029	8856	45
H(32A)	8823	1676	7666	90
H(32B)	8720	544	8209	90
H(32C)	10209	840	7905	90
H(34)	5278	5663	8201	33
H(35)	4571	7669	8685	38
H(36)	6288	9162	9159	40
H(37)	8684	8585	9156	43
H(38)	9395	6557	8683	39
H(39A)	7426	-988	546	81
H(39B)	6413	311	435	81