Asymmetric synthesis of phosphines via chiral cyclopalladium(II) complexes promoted reactions

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**ASYMMETRIC SYNTHESIS OF PHOSPHINES
VIA CHIRAL CYCLOPALLADIUM(II) COMPLEXES
PROMOTED REACTIONS**

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Abbreviations and Symbols

Ar	aryl
ax	axial
bn	benzyl
Bu	butyl
br	broad
ca.	about (Latin circa)
calcd	calculated
conc.	concentrated
cy	cyclohexyl
d	doublet, day(s)
dd	doublet of a doublet
ddd	doublet of a doublet of a doublet
ddt	doublet of a doublet of a triplet
dppe	1,2-bis(diphenylphosphino)ethane
dt	doublet of a triplet
de	diastereomeric excess
dec.	decomposed
deg	degree(s)
dm	decimeter
DMPP	3,4-dimethyl-1-phenylphosphole

ee	enantiomeric excess
eq	equatorial
Et	ethyl
et. al.	and others (Latin alii)
g	gram(s)
h	hour(s)
Hex	hexyl
Hz	hertz
i.e.	that is (Latin id est)
i	iso
m	multiplet, meta
Me	methyl
min	minute(s)
mp	melting point
n	straight chain
NMR	Nuclear Magnetic Resonance
NOE	Nuclear Overhauser Effect
o	ortho
p	para
Pr	propyl
Ph	phenyl
^{31}P NMR	$^{31}\text{P}\{^1\text{H}\}$ NMR
ppm	parts per million

q	quartet
qn	quintet
R	rectus (Latin: right absolute configuration)
ROESY 2D	rotating frame Nuclear Overhauser Enhancement
S	sinister (Latin: left absolute configuration)
s	singlet, secondary
t	triplet, tertiary
THF	tetrahydrofuran
tol	tolyl
Å	angstrom(s)
δ	NMR chemical shift in ppm
[α] _D	specific rotation measured at sodium D line (589 nm)

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SUMMARY

In this thesis, a systematic review of chiral phosphines and hydrophosphination reactions are described in Chapter 1. This chapter reviews the significance of chiral phosphines and their classification: chiral phosphines with P-chiral center(s), with chiral center(s) in the side-chain or axial chirality in the side-chain and chiral phosphines based on ferrocene. Their synthetic strategies are also discussed. In addition, acid catalyzed-, base catalyzed-, free radical mediated-, transition metal catalyzed-, transition metal complex promoted- and organocatalytic-hydrophosphination reactions are demonstrated.

In Chapter 2, a novel chiral resolution of the diphosphine ligand diethyl-1,2-bis-(diphenylphosphino)-ethanedicarboxylate with the assistance of an optically active palladium(II) template is thoroughly investigated. Through the interconversion of cationic diastereomeric mixtures from metal complexation, the optically active diphosphine was obtained in high yield.

In Chapter 3, an organopalladium(II) complex derived from (*S*)-N,N-dimethyl-1-(1-naphthyl)-ethylamine as the chiral auxiliary has been used to promote the asymmetric hydrophosphination reactions between diphenylphosphine and (*E*) or (*Z*)-diphenylphosphinostyrene in high regio- and stereoselectivities at low temperature with triethyl amine as external base. Optically active free ligand (*R*)-1,2-bis(diphenylphosphino)-1-phenylethane was obtained in high yield

subsequently. Mechanistic pathways explaining the stereoselectivity of the chiral organopalladium template promoted hydrophosphination reactions are also proposed.

In Chapter 4, an organopalladium complex containing ortho-metalated- (*R*)-(1-(dimethylamino)ethyl)naphthalene as the chiral auxiliary has been used to promote the asymmetric hydrophosphination reactions between diphenylphosphine and phenyldi[(*Z*)-prop-1-enyl]phosphine or phenyldi[(*E*)-prop-1-enyl]phosphine in high regio- and stereoselectivity under mild conditions. The hydrophosphination products were separated by fractional crystallization. The naphthylamine auxiliary could be removed chemoselectively by treatment with concentrated hydrochloric acid to form the corresponding optically pure neutral dichloro complexes. Subsequently, the dichloro complexes underwent ligand displacement with aqueous cyanide to generate the optically pure diphosphine ligands containing both phosphorus and carbon stereogenic centers in high yields.

In Chapter 5, the (1,1)- and (1,2)-addition of diphenylphosphine to 3-buten-2-one and ethyl propiolate is demonstrated. The hydrophosphination reactions were controlled chemoselectively by regulating the amount of triethylamine as the external base and in the presence of the chiral organopalladium(II) template derived from (*R*)-*N,N*-dimethyl-1-(1-naphthyl)ethylamine. The optically active diphosphines were obtained in high yields subsequently.

In Chapter 6, the asymmetric hydrophosphination reactions of diphenylphosphine and 2-(diphenylphosphino)-benzaldehyde or 2-(Diphenylphosphino)-*N*-phenyl benzamine promoted by an organopalladium(II)

complex derived from (*R*)-*N,N*-dimethyl-1-(1-naphthyl)-ethylamine as the chiral auxiliary proceeded in high regio- and stereoselectivities under mild conditions. The naphthylamine auxiliaries were removed chemoselectively from the addition products by treatment with concentrated hydrochloric acid to form the di-chloro complexes.

In Chapter 7, two converging synthetic pathways sharing a common metal template promoted asymmetric hydroalkoxylation and oxidation process have been illustrated for the synthesis of chiral bis-phosphine monoxide ligands. The vinylidene double bonds in coordinating products were highly activated towards the weak nucleophile methanol in the presence of an external mild base triethylamine, yielding adducts in high yields. The corresponding optically active ligand was liberated from chiral palladium template by replacement of strong chelating agent diphenylphosphono ethane (dppe).

Chapter 1

Introduction

1.1 General Properties of Phosphines

Tertiary phosphines, PR_3 , are important ligands in organic synthesis and organometallic chemistry by virtue of their unique properties.¹ Firstly, the electronic and steric properties of these ligands can be altered in a systematic and predictable way by varying the function groups. When they are coordinated to metal centers, the activities and selectivities of catalysts can be modified. Their electronic effects can be changed without changing steric effects [e.g., from PBu_3 to $\text{P}(\text{O}^i\text{Pr})_3$] or alternatively steric effects be changed without changing electronic effects [e.g., from PMe_3 to $\text{P}(o\text{-tolyl})_3$].² Secondly, these phosphines also stabilize a wide variety of metal ions of interest as complexes such as $(\text{PR}_3)_n\text{M-L}$. It is noteworthy that transition metal phosphine complexes are soluble in a wide range of organic media² and hence widely used in homogeneous catalytic reactions. Lastly, phosphorus-31 NMR spectroscopy is widely used in studying phosphine complexes. It has been of paramount importance in monitoring reactions by following the changes in bonding and stereochemistry that occur at phosphorus.³

Many developments have contributed to the growth of tertiary phosphine coordination chemistry and some of the more notable include the following: Wilkinson's homogeneous catalyst $\text{RhCl}(\text{PPh}_3)_3$,⁴ J. M. Styrer's copper hydride reagent $[\text{PPh}_3\text{CuH}]_6$,⁵ Vaska's Iridium Complex $\text{trans-IrCl}(\text{CO})(\text{PPh}_3)_2$ ⁶ and Cross

Coupling Reaction catalyst $\text{Pd}(\text{PPh}_3)_4$.⁷

1,2-Bis(diphenylphosphino)ethane (dppe) is one of the most used diphosphines. It can coordinate with platinum in complex **1**⁸ to form a catalyst or assist 1,1-reductive elimination from palladium in complex **2**.⁹ Misono used dppe to make a novel *trans*-dinitrogen complex of molybdenum **3**¹⁰ in 1969. Based on this finding, Schrock successfully did catalytic reduction of dinitrogen to ammonia at a single molybdenum center in 2003.¹¹ It is beyond doubt that the phosphine complexes are crucial to research in coordination chemistry and remain among the easiest examples to prepare.

1.2 Significance of Chiral Phosphines

Until the early 1970s, chemical access to optically active compounds from prochiral precursors remained a big challenge. The development of asymmetric synthesis by using homogenous catalysis provided a effective route to these enantiometrically pure substances.¹² Optically active phosphines have attracted great interest due to their use as ligands in transition metal catalysts for asymmetric reactions.¹³ Chiral phosphines were firstly used in homogenous asymmetric hydrogenation by Knowles¹⁴ and Horner¹⁵ in late 1960s. Since then, thousands of efficient chiral phosphorus ligands were developed.¹⁶ They are widely used in

asymmetric catalytic reactions such as hydrosilylation, hydroformylation, hydrocyanation, C=C bond migration and allylic substitution.¹⁷ Therefore, with the increasing demand for enantiomerically pure pharmaceuticals, agrochemicals, flavors, and other fine chemicals, transition metal catalysts with well-designed chiral phosphine ligands shall make continual significant impact in academy and industry, and the advance in this field should be of great significance.¹⁸

1.3 Various Class of Chiral Phosphines

Many developments have contributed to the growth of chiral phosphine chemistry and some of the more notable include the following: Knowles's P-chiral phosphine CAMP¹⁹ and the first P-chiral bisphosphine DIPAMP²⁰, Kagan's DIOP²¹, Burk's DuPhos²², Bosnich's ChiraPhos²³ and Noyori's BINAP.²⁴ Inspired by their work on phosphine chemistry, other research groups developed many other excellent chiral phosphine ligands. In acknowledgement of their contributions to chemistry, Knowles and Noyori were awarded the Nobel Prize in 2001 thus further highlighting the importance of this field.

1.3.1 Chiral Phosphines with P-Chiral Center(s)

The early development of optically active P-chiral phosphine ligands for chiral metal catalysts can be attributed to the studies of homogeneous asymmetric hydrogenation initiated by Knowles¹⁴ and Horner¹⁵ in the late 1960s. Although the first P-chiral bisphosphine DIPAMP has been proven to be a very efficient hydrogenation ligand, the development of new P-chiral bisphosphines continues to pose considerable challenges in preparation.

(*S,S*)-4

(*S,S*)-*t*-Bu-BisP*: R = *t*-Bu
(*S,S*)-Cy-BisP*: R = Cy

(*S,S*)-*t*-Bu-MiniPhos: R = *t*-Bu
(*S,S*)-Cy-MiniPhos: R = Cy
(*S,S*)-*i*-Pr-MiniPhos: R = *i*-Pr

(*S,S*)-Et-DuPhos: R = Et
(*S,S*)-*i*-Pr-DuPhos: R = *i*-Pr

(*S,S*)-Me-BPE: R = Me
(*S,S*)-Et-BPE: R = Et
(*S,S*)-*i*-Pr-BPE: R = *i*-Pr

RoPHOS

(*S,S*)-*i*-Pr-CnrPhos: R = *i*-Pr
(*S,S*)-Cy-CnrPhos: R = Cy

(*S,S*)-*i*-Pr-BPE-4: R = *i*-Pr
(*S,S*)-Cy-BPE-4: R = Cy

5

A series of chiral tertiary phosphines and arsines including (*S,S*)-**4** were attained by Wild by method of resolution with chiral metal complexes.²⁵ Several other P-chiral bisphosphines such as BisP*²⁶ and MiniPhos²⁷ have been developed by Imamoto. Subsequently, the development of P-chiral phosphorus ligands regained much attention.

In the early 1990s, Burk introduced a new series of efficient bisphospholane ligands DuPhos and BPE.²⁸ Inspired by the success of DuPhos and BPE, many other phosphorus ligands based on the structural variations have been developed, such as CnrPHOS²⁹, RoPHOS³⁰ and **5**³¹.

1.3.2 Chiral Phosphines with Chiral Center(s) in the Side-chain

Bisphosphines with one chiral carbon center have been shown to be effective ligands in asymmetric hydrogenation of prochiral olefins.³² It has been demonstrated that a single chiral center may control the stereochemistry of these catalytic reactions when phosphine coordinated with metal to form a rigid five-membered chelate ring.³³ ProPhos³⁴, CycPhos³⁵, PhenPhos³⁶ are typical examples of this group of phosphines. Several excellent chiral *C*₂-symmetric chelating bisphosphines were also discovered. These include BDPP³⁷, NorPhos³⁸, DPCP³⁹, CBD⁴⁰, PyrPhos⁴¹ and **6**⁴². Most of them are 1,2-bisphosphines. However, 1,3-bisphosphines are relatively few, such as BDPP and PPCP⁴³. In addition, CyDIOP⁴⁴ and DIOPCP⁴⁵ were prepared based on the structural variations of Kagan's DIOP.

1.3.3 Chiral Phosphines with Axial Chirality in the Side-chain

The atropisomeric C_2 -symmetrical bisphosphine BINAP²⁴ was first reported by Noyori in 1980. It was found that BINAP-Ru complexes are efficient catalysts for asymmetric hydrogenation of various functionalized olefins⁴⁶ and ketone⁴⁷, and even some unfunctionalized ketones⁴⁸. Since then, many other atropisomeric chiral bisphosphines have been developed based on modification of the electronic and steric properties of BINAP. These include H₈-BINAP⁴⁹, SEGPHOS⁵⁰, MeO-NAPhePHOS⁵¹ and more. Inspired by the success of BINAP, BICHEP⁵² were developed by Miyashima; BIPHEMP⁵³ and MeO-BIPHEP⁵⁴ were developed by Schmid. BIMOP⁵⁵, MOC-BIMOP⁵⁶ and FUPMOP⁵⁷ were successfully prepared by Achiwa.

(S)-H₈-BINAP

(S)-MeO-NAPhePHOS

(S)-SEGPHOS

(S)-BICHEP: R = Cy; R' = CH₃
 (S)-BIPHEMP: R = Ph; R' = CH₃
 (S)-MeO-BIPHEP: R = Ph; R' = OCH₃

(S)-BIMOP: R = Ph
 (S)-MOC-BIMOP: R = Cy

(S)-FUPMOP

XPhos

(S)-BisbenzodioxanPhos

SPhos

1.3.4 Chiral Phosphines Based on Ferrocene

Another important class of chiral phosphines is those with planar chirality in the side-chain based on the backbone of ferrocene. Some successful ligands include non-*C*₂-symmetrical ferrocene-based bisphosphines Josiphos⁵⁸ and TaniaPhos⁵⁹ and *C*₂-symmetrical ferrocene-based bisphosphine FerroPhos⁶⁰. These ligands have been effectively used in Rh-catalyzed asymmetric hydrogenations.

1.4 Synthetic Strategies for Preparation of Chiral Phosphines

Since the two chiral forms of a phosphine ligand have identical chemical and physical properties in the absence of an external chiral influence, the synthesis of one optically active phosphine must involve a chiral source. Generally, the preparation of chiral phosphines can be divided into the following three categories:

1.4.1 Resolution

Until the early 1970s, the conventional resolution of racemates was the primary method used to obtain optically active compounds. A solution of the racemic mixture interacts with an optically pure compound to form a mixture of diastereomers. Unlike enantiomers, diastereomers have different physical

properties and thus can usually be easily separated by means of fractional crystallization or chromatography, and then treated separately to liberate each enantiomer. Chiral resolution is an important approach to optically active materials due to the ease of preparing racemic substrates. The well known C_2 -symmetrical atropisomeric diphosphine BINAP was first prepared by Noyori in its enantiomerically pure form by means of resolution⁶¹ (Scheme 1.1).

Scheme 1.1

A series of chiral tertiary phosphines and arsines were attained by Wild using the same approach²⁵. An example is shown in Scheme 1.2.

Scheme 1.2

1.4.2 Transformation

Other methods involve transformation or derivatization of readily available natural chiral compounds, such as amino acid, tartaric and lactic acids, terpenes, carbohydrates and alkaloid. It is the most obvious way to obtain a chiral compound since it modifies an appropriate chiral precursor from a natural source in several chemical steps to form the final product. Normally, there is no new chiral center formed in the process. The chiral center(s) of product is preserved or inverted from the starting materials. Optically active DIOP²¹ and PhenPhos³⁶ are both prepared by using this method (Scheme 1.3 and 1.4).

Scheme 1.3

Scheme 1.4

1.4.3 Asymmetric Synthesis

One approach is chiral auxiliary-controlled synthesis. The chirality is transferred intramolecularly by chiral center(s) present in the auxiliary. However, stoichiometric amount of chiral auxiliary are required for the process. Another approach is the catalyzed asymmetric synthesis⁶², an example of chiral phosphine platinum complex catalyzed reaction is illustrated in Scheme 1.5.

Scheme 1.5

1.5 Hydrophosphination Reactions

The asymmetric synthesis of functionalized optically active phosphines *via* the addition of phosphorus-hydrogen bonds to carbon-carbon multiple bonds is an important reaction in organophosphorus chemistry. Hydrophosphination reaction can proceed with the assistance of acids, bases, radical initiators, transition metal catalysts organocatalysts and transition metal templates.

1.5.1 Simple Hydrophosphination Reactions

The simple hydrophosphination reaction discussed here does not involve any external promoters. As illustrated in Scheme 1.6, diphenylphosphine reacts readily

with dimethyl acetylenedicarboxylate (DMADC) in ether.⁶³ This example shows that activation of the acetylenic bond by electron-withdrawing groups facilitates the hydrophosphination reaction.

Scheme 1.6

Hydrophosphination reaction can also proceed by thermal pathway in case the acetylenic bond is not activated. Phenylacetylene **12** reacts with diphenylphosphine at 100 °C for four days yielding *cis*-styryldiphenylphosphine **13** as major product (Scheme 1.7).⁶⁴ It is noteworthy that the addition reaction proceeds regioselectively to give only anti-Markovnikov product.

Scheme 1.7

Another addition reaction yielding anti-Markovnikov product is shown in Scheme 1.8.⁶⁵ Bisphosphine monoxide (BPMO) **15** is prepared by the hydrophosphination reaction of di-*n*-butylphosphine with di-*n*-butylethynylphosphine oxide **14** at 80 °C.

Scheme 1.8

The hydrophosphination reaction can also proceed with neat reagents (Scheme 1.9).⁶⁶ When 1 *eq* of diphenylphosphine is added to 1 *eq* of cinnamaldehyde **16**, the

addition reaction of the P-H moiety to olefinic bond happens exclusively, giving quantitative formation of the new tertiary phosphine **17**. When 2 *eq* of diphosphine is added to 1 *eq* of cinnamaldehyde **16**, hydrophosphination of both the C=C and C=O bonds takes place to give the phosphine derivative **18**. In most organic solvents the hydrophosphination of the C=O group is reversible, leading to a dynamic equilibrium between **17** and **18**. However compound **18** is stable in coordinating solvents such as DMSO, DMF, and pyridine.

Scheme 1.9

1.5.2 Acid-Catalyzed Hydrophosphination Reactions

In the absence of a catalyst, heating a mixture of di-*tert*-butylphosphine and methyl vinyl ether **19** to above 130 °C for several hours yields the Markovnikov product di-*tert*-butyl(1-methoxyethyl)- phosphine **20**. This product is different from the expected base- or radical-catalyzed anti-Markovnikov product di-*tert*-butyl(2-methoxyethyl)- phosphine **21** (Scheme 1.10).⁶⁷ Adding catalytical amounts of acid to the mixture greatly reduces the reaction time.

Scheme 1.10

Similarly, diethylphosphine reacts with methyl vinyl ether and acid to yield diethyl (1-methoxyethyl)-phosphine **22**. Using the same reagents and a radical initiator, the reaction is regioselective for another addition product, diethyl (1-methoxyethyl)-phosphine **23** (Scheme 1.11).⁶⁷

Scheme 1.11

The *trans* addition product ethyl carboxylate substituted phosphine **25** can be prepared efficiently from the reaction between diphenylphosphine and ethyl propiolate **24** at room temperature in dichloromethane with 1 *eq* acetic acid (Scheme 1.12).⁶⁸ The acetic acid in the reaction provides a weak acidic reaction medium to inhibit the side polymerization of methyl propiolate since it is recognized that the propiolate polymerizes readily in basic medium.

Scheme 1.12

1.5.3 Base-Catalyzed Hydrophosphination Reactions

Unlike acid-catalyzed hydrophosphination reactions, base-catalyzed additions of primary and secondary phosphines to activated alkenes are well established. These reactions are believed to involve the following steps: first, protonolysis of P-H bond with the assistance of base to give corresponding phosphide anion; second, the nucleophilic phosphide anion undergoes nucleophilic (Michael) addition to alkene; finally, protonolysis to give the products.

As illustrated in Scheme 1.13, the use of *t*-BuOK in DMSO allows a smooth addition of diphenylphosphine to various functionalized alkenes **26** leading to polyfunctional phosphines **27** in good yields.⁶⁹

Scheme 1.13

The base-catalyzed addition of diphenylphosphine with diarylethynes **28** yields diphosphine **29** as product (Scheme 1.14).⁷⁰ As shown in Scheme 1.6 previously, activated alkynes with electron-withdrawing groups could undergo hydrophosphination reaction without external promoters, such as base. However, in this case as shown in Scheme 1.14, external base is needed.

Scheme 1.14

A triphosphine ligand 1,1,2-tris(diphenylphosphino)ethane **31** is synthesized by refluxing 1,1-bis(diphenylphosphino)ethene **30**, diphenylphosphine and a catalytic amount of potassium *tert*-butoxide in THF in our group as presented in Scheme 1.15.⁷¹

Scheme 1.15

1.5.4 Free Radical-Mediated Hydrophosphination Reactions

A free radical-initiated addition of phosphine to C=C double bonds of **32** is illustrated in Scheme 1.16.⁷² Azobisisobutyronitrile (AIBN) is used as radical initiator in the reaction, giving primary **33**, secondary **34** and tertiary phosphines **35** in yields varying from 4 to 83%.

Scheme 1.16

As shown in Scheme 1.17, secondary phosphines **37** react readily with *N*-vinylpyrroles **36** under radical initiation of AIBN to give regiospecifically anti-Markovnikov adducts, diorganyl-2-(1-pyrrolyl)ethylphosphines **38** in high yields.⁷³

Scheme 1.17

1.5.5 Transition Metal-Catalyzed Hydrophosphination Reactions

The first example of intermolecular hydrophosphination of styrenes catalyzed by Ni and Pd complexes is presented in Scheme 1.18.⁷⁴ The reaction of diphenylphosphine with styrene, 4-vinylpyridine, 2-vinylpyridine, 4-methoxystyrene, 2-methoxystyrene, and 5-vinyl-2-methylpyridine in benzene under Ni[P(OEt)₃]₄ catalysis proceeds with high yields and selectivity to give only anti-Markovnikov products **40**.

Ar = Ph, 2-Py, 4-Py, 5-(2-MePy), 2-MeOPh, 4-MeOPh

catalyst
 a, Ni(PPh₃)₂Br₂
 b, Ni[P(OEt)₃]₄
 c, Pd(CH₃CN)₂Cl₂

Scheme 1.18

A possible mechanism of hydrophosphination is presented in Scheme 1.19. Firstly, oxidative addition of the P-H moiety to Ni takes places, forming Ni-H and Ni-P bonds. Secondly, alkenes **39** insert into the Ni-H bond. Finally, reductive elimination happens to give the addition products **40**.

Scheme 1.19

Hydrophosphination of 1-alkynylphosphines **41** with diphenylphosphine proceeds with copper catalysis and is illustrated in Scheme 1.20.⁷⁵ The reaction provides an easy and efficient access to a variety of (*Z*)-1,2-diphosphino-1-alkenes **42** and their sulfides **43**. This reaction is highly chemoselective and can be performed even in an aqueous medium.

Scheme 1.20

Subsequently, trivalent diphosphines **42** could be obtained from radical reduction of the diphosphine disulfides **43** with tris(trimethylsilyl)silane (Scheme 1.21).

Scheme 1.21

The C=C double bonding compounds **42** and **43** can undergo further transformation. As illustrated in Scheme 1.22, enantioselective hydrogenation of (Z)-3,3-dimethyl-1,2-bis(diphenylthiophosphinyl)-1-butene **43b** followed by desulfidation leads to a chiral bidentate phosphine ligand **45**.

Scheme 1.22

An example of asymmetric addition of secondary phosphine to C=C double bond with chiral nickel catalyst is presented in Scheme 1.23.⁷⁶ Hydrophosphination of methacrylonitrile **46** gives optically enriched addition product **47** in 45 to 89% ee.

Scheme 1.23

1.5.6 Organocatalytic Hydrophosphination Reactions

Chiral phosphines are highly valuable ligands for metal-catalyzed asymmetric synthesis and can be used as catalysts in organocatalytic reactions. However, organocatalytic hydrophosphination reactions are less studied. Two unprecedented examples of highly chemo- and enantioselective organocatalytic hydrophosphination of α,β -unsaturated aldehydes **48** are illustrated in Scheme 1.24⁷⁷ and 1.25⁷⁸. The reactions are catalyzed efficiently by simple chiral pyrrolidine derivatives **51** – **57** and give the corresponding phosphine derivatives **49** in high yields and with 12 to 99% ee. Comparing with a metal-catalyzed process, an organocatalytic approach prevents product inhibition arising from the coordination ability of the phosphorus atom.

Scheme 1.24

Scheme 1.25

Another example of organocatalytic hydrophosphination reaction is shown in Scheme 1.26.⁷⁹ Hydrophosphination of nitroalkene **58** with organocatalysts **61-64** gives β -nitrophosphines **59** in high yields with 15 to 67% ee.

Scheme 1.26

1.5.7 Transition Metal Complex Promoted Hydrophosphination Reactions

When diphenylphosphine coordinates to a transition metal complex, the P-H bond is normally activated. In most cases, metal complex promoted hydrophosphination reaction takes place in mild conditions. Newly formed phosphines are protected as they are coordinated with metal centers. When chiral metal templates are applied in reactions, diastomeric enriched complexes are formed. Optically active compounds are obtained subsequently by fractional crystallization or column chromatography. Finally, chiral phosphines are liberated from the metal auxiliaries chemoselectively.

Iron complexes promoted hydrophosphination reactions between dimethyl

acetylenecarboxylic ester (DMADC) with 1 *eq* and 2 *eq* of diphenylphosphine are illustrated in Scheme 1.27 and 1.28.⁸⁰

Scheme 1.27

Scheme 1.28

As shown in Scheme 1.29, chromium and molybdenum complexes promoted addition reaction of diphenylphosphine and functionalized alkynes **70** give five-membered ring diphosphine chelating products **71**.⁸¹

Scheme 1.29

These reactions are believed to be a type of Michael addition (Scheme 1.30), proceeding *via* carbonion intermediates and involve the following steps: first, protonolysis of P-H bond with the assistance of BuLi to give corresponding

phosphide anion; second, the phosphide anion undergoes nucleophilic (Michael) addition to acetylene to give a carbonion; third, the carbonion abstracts a proton from the neighboring phosphine and the sequence then repeat itself; finally, protonation on workup gives the resulting product.

Scheme 1.30

An organopalladium complex (*S*)-**72** containing ortho-metalated (*S*)-(1-(dimethylamino)-ethyl)-naphthalene as the chiral auxiliary has been used to promote the asymmetric hydrophosphination reactions between diphenylphosphine and (*E*)- or (*Z*)-diphenyl-1-propenylphosphine in our group (Scheme 1.31).⁸² The reactions proceed with high regio- and stereoselectivities under mild conditions. The new formed chelating diphosphine is obtained as free ligand in its optically pure form by a two-step transformation.

Scheme 1.31

As illustrated in Scheme 1.32⁸³ and 1.33⁸⁴, organopalladium complex promoted hydrophosphination reactions between diphenylphosphine and 3-diphenylphosphanyl-but-3-en-1-ol or dimethyl acetylenecarboxylic ester (DMADC) have been demonstrated previously by our group. The newly formed chelating diphosphines are obtained as free ligands in their optically pure forms by two-step transformations. The hydrophosphination of functionalized alkene and alkyne are thus demonstrated.

Scheme 1.32

Scheme 1.33

1.6 Bisphosphine monoxides

Bisphosphine monoxides (BPMO) have proven to be successful soft/hard ligands for hydroformylation⁸⁵, carbonylation⁸⁶ and more.⁸⁷ Due to the presence of both the soft (P) and hard (O) Lewis base centers on one ligand, BPMOs can stabilize various transition metals in low and high oxidation states. In addition, their labile chelating properties made BPMO quite useful in organometallic chemistry and catalytical chemistry.⁸⁸

Two general synthetic strategies are known for the preparation of BPMOs. One involves assembling two phosphorus units to form a BPMO molecule. The other approach is selective oxidation of polyphosphines. Charette synthesized BozPhos⁸⁹ from DuPhos (Scheme 1.34) and Grushin prepared (S)-BINAP(O), Tol-BINAP(O), dppeO, dppmO, dmpmO, dppbzO, **81** and **82** by Pd-catalyzed selective oxidation (Scheme 1.35).⁹⁰

Scheme 1.34

Scheme 1.35

1.7 Aim of the Present Project

Over the past few years, our group has reported the use of chiral cyclometalated-amine complexes (*S*)-**7**, (*S*)-**72** and (*S*)-**79** as efficient promoters for asymmetric synthesis of chiral phosphines by means of the Diels–Alder reactions,⁹¹ hydroamination reactions,⁹² hydrophosphination reactions^{82–84} and hydroarsination reactions.⁹³ Their roles as resolving agents for conventional resolution⁹⁴ and kinetic resolution⁹⁵ have also been studied. The objective of this project work is to further investigate the application of these organometallic complexes on hydrophosphination reactions, hydroalkoxylation reactions and selective oxidation reactions in order to synthesize a wider range of functional phosphine ligands.

In chapter 2 (Scheme 1.36), a novel and simple resolution approach for the preparation of a diester-substituted diphosphine involving interconversion between diastereomeric complexes will be presented. Through the interconversion of cationic diastereomeric mixtures, the optically active diphosphine is obtained in high yield.

Scheme 1.36

Although chiral cyclometalated-amine complexes (*S*)-72 and (*S*)-79 have been successfully applied to hydrophosphination reactions by our group,⁸²⁻⁸⁴ a wider spectrum of their applications is expected. In chapters 3-6, hydrophosphination reactions between diphenylphosphine and functionalized alkenes (Scheme 1.37-1.39), alkynes (Scheme 1.40-1.41), aldehyde (Scheme 1.42) and imine (Scheme 1.43) will be studied. The corresponding newly formed functional bidentate phosphine ligands will be liberated in their optically pure form.

Chapter 3

Scheme 1.37

Chapter 4

Scheme 1.38

Chapter 4

Scheme 1.39

Chapter 5

Scheme 1.40

Chapter 5

Scheme 1.41

Chapter 6

Scheme 1.42

Chapter 6

Scheme 1.43

Optically pure bisphosphine monoxides (BPMOs) are relatively rare compared to other type of phosphine ligands. In chapter 7, asymmetric synthesis of a chiral mixed phosphine-phosphine oxide ligand *via* hydroalkoxylation reaction and selective oxidation reaction will be reported (Scheme 1.44).

Chapter 7

Scheme 1.44

Chapter 2

A Novel Chiral Resolution of Diethyl-1,2-bis-(diphenylphosphino)-ethanedicarboxylate Involving Metal Complexation and Interconversion Between Diastereomeric Palladium (II) Salts

2.1 Introduction

Enantiomerically pure tertiary phosphines have been considered as one of the most effective ligands for most homogeneous transition-metal catalysts.^{18, 96} They influence reaction efficiency in terms of catalytical activity and enantioselectivity. Despite the increasing demand for these useful compounds in many aspects of science such as asymmetric catalysis,⁹⁷ pharmaceuticals⁹⁸ and biochemistry,⁹⁹ the preparation of these reactive and potentially unstable chiral ligands remains a major challenge.

Chiral resolution is an important approach to these optically active materials due to the ease of preparing racemic substrates. The well known C₂-symmetrical atropisomeric diphosphine BINAP was first prepared by Noyori in its enantiomerically pure form by means of resolution.^{24a} A series of chiral tertiary phosphines and arsines were attained by Wild using a similar approach.¹⁰⁰ Kinetic resolution is another well established method.¹⁰¹ However, one drawback with these methods is that the maximum yield of each enantiomer is only 50%. Recently,

dynamic kinetic resolution (DKR) has been developed to overcome this limitation. In DKR, racemic starting material can be transformed into one enantiomer when racemization occurs concurrently.¹⁰² Nevertheless, in a successful dynamic kinetic resolution, both the inversion and resolution steps have to be carefully tuned.¹⁰³ For these considerations, a more facile resolution approach would be helpful for the synthesis of new chiral phosphines.

A conceptual basis for the three different resolution approaches in which the enantiomers **A** and *epi-A* are separated by chiral resolving agent **B*** is illustrated in Scheme 2.1. Normally, **A** and *epi-A* coordinate with **B*** to form diastereomers **AB*** and *epi-AB**. In a classic kinetic resolution, the resolution is achieved through unequal reaction rates of enantiomers with a chiral agent.¹⁰⁴ In DKR, the high yield of desired isomer is obtained through interconversion between enantiomers **A** and *epi-A*.¹⁰⁵ If the diastereomeric complexes **AB*** and *epi-AB** can equilibrate under certain condition, it may then be possible to obtain the desired optically pure isomer **A** or *epi-A* with greater than 50% yield.¹⁰⁶

Scheme 2.1

Over the past few years, our group has reported the use of chiral cyclometalated-amine complexes as efficient promoters for asymmetric synthesis of chiral phosphines by means of Diels–Alder reactions,⁹¹ hydroamination reactions,⁹² hydrophosphination reactions^{82–84} and hydroarsination reactions.⁹³ Their roles as resolving agents for conventional resolution⁹⁴ and kinetic resolution⁹⁵ have also been studied. In this chapter, we present a novel and simple resolution approach for the preparation of a di-substituted diphosphine involving interconversion between diastereomeric complexes.

2.2 Results and Discussion

2.2.1 Ligand Synthesis. The diester-substituted ligands (*S, S*)-**84** and (*R, R*)-**84** were prepared as a mixture of enantiomers by literature method.⁶³ They were further purified by silica gel chromatography. The ³¹P NMR spectrum in CDCl₃ exhibited only one sharp singlet at δ -6.4. This indicated that no meso compound (*S, R*)-**84** was present in the racemic ligand (Scheme 2.2).

Scheme 2.2

2.2.2 Formation and Interconversion of Diastereomers.

The resolution of (*S*, *S*)- **84** and (*R*, *R*)- **84** was based on the separation of pairs of internally diastereomeric palladium (II) salts derived from the resolving agent bis(acetonitrile) $\{(S)-1-[1-(\text{dimethylamino})\text{-ethyl}]-2\text{-phenyl-}C,N\}$ palladium(II) perchlorate, (*S*)-**7**;¹⁰⁷ bis(acetonitrile) $\{(S)-1-[1-(\text{dimethylamino})\text{ethyl}]-2\text{-naphthalenyl-}C, N\}$ palladium(II) perchlorate, (*S*)-**79**^{94a, 108} and bis(acetonitrile) $\{(S)-3-[1-(\text{dimethylamino})\text{ethyl}]-2,7\text{-dimethyl-4-naphthalenyl-}C,N\}$ palladium(II) perchlorate, (*S*)-**85** which is relatively new (Scheme 2.3).

Scheme 2.3

Scheme 2.4

The optically active perchlorate salt (*S*)-**85** was converted quantitatively from the dimeric complex (*S*)-**86**¹⁰⁹ by treatment with silver perchlorate in acetonitrile, $[\alpha]_{\text{D}}$

+268 (c 0.5, CH_2Cl_2) (Scheme 2.3.1). X-ray structural analysis of the cationic complex (*S*)-**85** was achieved (Figure 2.1). Selected bond lengths and angles are given in Table 2.1. The methyl group at the *S*-chiral carbon centre is located at the axial position while the five-membered palladacycle adopts a λ conformation with C(12) and C(13) lying 0.53 and 0.89 Å respectively out of the coordination plane. The geometry at palladium is distorted square planar with *cis* angles ranging between 80.4(1) and 96.6(1) °. The palladium coordination distances are unexceptional, though the Pd-N bond [2.117(4) Å] *trans* to carbon is significantly longer than those *trans* to nitrogen [2.055(3) and 2.018(3) Å]. The naphthalene ring has a slightly twisted conformation, with deviation from planarity of up to 0.12 Å; the palladium atom lies 0.42 Å from this plane.

Figure 2.1. Molecular structure and absolute stereochemistry of complex (*S*)-**85**

Table 2.1. Selected Bond Lengths (Å) and Angles (deg) for (*S*)-**85**

Pd(1)-C(1)	1.992(3)
Pd(1)-N(1)	2.055(3)
Pd(1)-N(2)	2.117(4)
Pd(1)-N(3)	2.018(3)
C(1)-Pd(1)-N(3)	95.7(1)
C(1)-Pd(1)-N(1)	80.4(1)
N(3)-Pd(1)-N(1)	174.0(2)
C(1)-Pd(1)-N(2)	177.0(1)
N(3)-Pd(1)-N(2)	87.2(1)
N(1)-Pd(1)-N(2)	96.6(1)

The initial mixture of diastereomers in each resolution process was obtained from one equivalent of racemic ligand and one equivalent each of the three resolving agents (*S*)-**7**, (*S*)-**79** and (*S*)-**85** in dichloromethane (Scheme 2.5-2.7). The formation of the initial diastereomers were monitored by the ^{31}P NMR spectroscopy in CDCl_3 and were found to be complete in 10 minutes to give a 1:1 mixture of diastereomers in high yields. The ^{31}P NMR spectrum of each diastereomer exhibited a pair of doublets. As shown in Scheme 2.5, when (*S*)-**7** was used as the resolving agent, the ^{31}P NMR spectrum of the initial 1:1 mixture of (*S*, *RR*)-**87** and (*S*, *SS*)-**87** exhibited two pairs of doublets at δ 35.7, 55.4 ($J_{\text{PP}} = 38$ Hz) and 34.8, 55.6 ($J_{\text{PP}} = 39$ Hz), respectively. The cationic diastereomeric mixture was then treated with two equivalent of triethyl amine and stirred for 16h. The ^{31}P NMR spectrum exhibited the same two pairs of doublets, but in a ratio of 3:1 with (*S*, *RR*)-**87** being the major product.

Scheme 2.5

Similarly, when the naphthylamine complex (S)-79 was used as the resolving agent, the ³¹P NMR spectrum of the initial 1:1 mixture of (S,RR)-88 and (S,SS)-88 exhibited two pairs of doublets at δ 35.3, 54.8 ($J_{\text{PP}} = 39$ Hz) and 35.6, 56.4 ($J_{\text{PP}} = 38$ Hz) respectively. After overnight stirring with triethyl amine, the ratio changed to 6:1 with (S,RR)-88 being the major product (Scheme 2.6). Furthermore, the ratio of (S,RR)-88 and (S,SS)-88 changed to 8:1 and 10:1 upon changing the solvent to tetrahydrofuran and methanol, respectively.

Scheme 2.6

As illustrated in Scheme 2.7, when the sterically demanding complex (*S*)-**85** was used as the resolving agent, the ^{31}P NMR spectrum of the initial 1:1 mixture of (*S*, *RR*)-**89** and (*S*, *SS*)-**89** exhibited two pairs of doublets at δ 32.7, 45.3 ($J_{\text{PP}} = 41$ Hz) and 30.1, 42.6 ($J_{\text{PP}} = 45$ Hz) respectively. After overnight stirring with triethyl amine, only one pair of doublets remained at δ 32.7, 45.3 ($J_{\text{PP}} = 41$ Hz) while the signals of complex (*S*, *SS*)-**89** disappeared completely. It is noteworthy that without triethyl amine, the ratio of diastereomeric complexes in each reaction remains 1:1. Therefore the change of chirality at the chiral carbon centers is attributed to the removing and replacement of hydrogen atoms at these centers (CHCOOEt) with the aid of triethyl amine. In this way, the diastereomeric complexes equilibrate under the mild base condition.

Scheme 2.7

As illustrated in Figure 2.2, the high stereoselectivity observed after addition of base can be explained through absolute conformation of the cationic diastereomers. In chiral cyclopalladated complexes (S)-79 and (S)-85, the methyl groups at the S-chiral carbon centers are located at the axial positions while both the five-membered palladacycles (PdCN rings) adopt λ conformation. This conformation is maintained even after these complexes coordinate with the racemic ligands. When these complexes coordinate with (R,R)-84, new five-membered palladacycles (PdPP rings) formed also adopted the λ conformation (absolute conformation **A**) while when coordinated with (S,S)-84 it adopted δ conformation (absolute conformation **B**). Absolute conformation **A** is sterically more favorable than **B** due to the repulsion existing between neighboring groups.

Figure 2.2

The organometallic ring conformation of complex (*S*)-**7** is not locked and the puckered ring undergoes rapid interconversion between δ and λ conformations in solution. In solid state, both δ and λ conformations are also frequently found in (*S*)-**7** derivatives. However, in complex (*S*)-**79**, there is a strong steric inter-locking force existed between the methyl group at the chiral carbon centre and the neighboring H(8) of the naphthylenyl ring. The crystallographic determinations and rotating overhauser effect (ROSEY) NMR investigations confirmed that the organometallic ring in (*S*)-**79** is indeed locked into the static λ conformation, both in the solid state and in solution. Thus the prochiral NMe₂ moiety are fixed into the non-equivalent axial and equatorial positions and thus control the stereochemistry of the neighboring coordination sites. Similarly, in complex (*S*)-**85**, there is a strong steric inter-locking force operating between the methyl group at the chiral carbon centre and the neighboring methyl group, Me(11). Furthermore, the

aromatic hydrogen atom H(3) is introduced adjacent to the Pd–C bond to exert stereochemical influence on the coordination position *trans* to the NMe₂ moiety. These explains why the ratio change with different chiral metal templates is (S)-**85** > (S)-**79** > (S)-**7**.

2.2.3 Liberation of Resolved Diphosphine. As discussed earlier, when the sterically demanding resolving agent (S)-**85** was used to form the diastereomers, only complex (S, SS)-**89** was remaining in solution after the diastereomeric mixture was treated with Et₃N. This solution was then treated with concentrated hydrochloric acid to remove chiral amine auxiliary chemoselectively (Scheme 2.7). The ³¹P NMR spectrum of the dichloro complex in CDCl₃ showed a sharp singlet at δ 57.2. The neutral dichloro complex (R, R)-**90** crystallized from dichloromethane and diethyl ether as yellow prisms in its optically pure form, [α]₄₃₅ +144 (*c* 0.3, CH₂Cl₂).

The molecular structure and the absolute stereochemistry of (R, R)-**90** were determined by X-ray crystallography (Figure 2.3). Selected bond lengths and angles are given in Table 2.2. The five-membered chelate ring has the asymmetric skew conformation of λ helicity with both both ester substituents on the asymmetric carbon centers of *R* absolute configuration occupying equatorial sites.

It is noteworthy that after treatment of 3:1 and 10:1 internally cationic diastereomeric mixtures derived from the resolving agent (*S*)-**7** and (*S*)-**79** respectively with concentrated hydrochloric acid, (*R, R*)-**90** could also be obtained by fractional crystallization of the enantiometric mixtures from dichloromethane and diethyl ether as major isomer.

Subsequently, the dichloro complex (*R, R*)-**90** undergo ligand displacement with aqueous cyanide at room temperature to generate (*R, R*)-diethyl-1,2-bis-(diphenylphosphino)-ethanedicarboxylate, (*R, R*)-**84** in its optically pure form in high yield, $[\alpha]_D -275$ (*c* 0.6, CHCl_3). The ^{31}P NMR spectrum of the dichloro complex in CDCl_3 exhibited a sharp singlet at δ -6.4.

The optical purity of (*R, R*)-**1** was reconfirmed by recoordination of this released ligand to one equivalent of chiral cyclopalladated complexes (*S*)-**7**, (*S*)-**79** and (*S*)-**85**. The ^{31}P NMR spectrum of the each crude product exhibited only a pair of doublets. These signals are identical to (*S, RR*)-**87**, (*S, RR*)-**88** and (*S, RR*)-**89** respectively.

2.3 Conclusion

In conclusion, the chiral resolution of a diester-substituted diphosphine was demonstrated. Through the interconversion of cationic diastereomeric mixtures, the optically active diphosphine was obtained in high yield. Further investigation is currently underway to prepare chiral ligands containing Arsenic and Nitrogen atoms.

2.4 Experimental Section

Reactions involving air-sensitive compounds were performed under a positive pressure of purified 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 0.1dm cell at 25 °C with a Perkin-Elmer model 341 polarimeter. Elemental analyses were performed by the staff in the Elemental Analysis Laboratory of the Division of Chemical and Biological Chemistry of Nanyang Technological University. Melting points were measured using the SRS Optimelt Automated Melting Point System, SRS MPA100.

All solvents used for the 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(acetonitrile) [(*S*)-1-[1-(dimethylamino)ethyl]-2-phenyl-*C*, *N*]-palladium(II) perchlorate ((*S*)-7)¹⁰⁷ and bis(acetonitrile)[(*S*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-*C*, *N*]-palladium(II) perchlorate ((*S*)-79)^{94a, 108} 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 cyanide compounds.

Synthesis of {(*S*)-3-[1-(dimethylamino)ethyl]-2,7-dimethyl-4-naphthalenyl-*C*, *N*} palladium(II) perchlorate, (*S*)-85. Complex (*S*)-86 (2.00 g) in dichloromethane (60 mL) and aqueous silver perchlorate (1.35 g) were stirred

vigorously at room temperature for 2 h. The mixture was filtered through Celite (to remove AgCl), washed with water (3×30 mL), and dried (MgSO_4) and subsequently crystallized from dichloromethane and n-hexane as yellow prisms: 2.43 g (87% yield); mp 160–162 °C (dec); $[\alpha]_{\text{D}} +268$ (c 0.5, CH_2Cl_2). Anal. Calcd for $\text{C}_{20}\text{H}_{26}\text{ClN}_3\text{O}_4\text{Pd}$: C, 46.7; H, 5.1; N, 8.2. Found: C, 46.9; H, 4.9; N, 8.2. ^1H NMR (CDCl_3) δ 2.09 (d, 3 H, $J_{\text{HH}} = 6.4$ Hz, CHMe), 2.30 (s, 3 H, ArMe), 2.37 (s, 3 H, ArMe), 2.38 (s, 3 H, NCMe), 2.47 (s, 3 H, NCMe), 2.73 (s, 3 H, NMe), 2.74 (s, 3 H, NMe), 3.73 (q, 1 H, $J_{\text{HH}} = 6.4$ Hz, CHMe), 7.18–7.93 (m, 4 H, aromatics).

Synthesis of (*R, R*)-Dichloro-[diethyl-1,2-bis-(diphenylphosphino)-ethane dicarboxylate]palladium (II), (*R, R*)-90. Complex (*S*)-85 (0.50 g) and racemic ligand diethyl-1, 2-(diphenylphosphino)-1, 2-ethanedicarboxylate (0.50 g) in dichloromethane (30 mL) was stirred at room temperature for 10 min, triethyl amine (0.20 g) was added and stirred for 16 h. Concentrate hydrochloric acid (10 mL) was added and stirred vigorously for 12 h. The reaction mixture was washed with water (3×20 mL), and dried (MgSO_4) and subsequently crystallized from dichloromethane and diethyl ether as yellow crystals: 0.46 g (59% yield); mp 233–234 °C; $[\alpha]_{435} +144$ (c 0.3, CH_2Cl_2); Anal. Calcd for $\text{C}_{32}\text{H}_{32}\text{Cl}_2\text{O}_4\text{P}_2\text{Pd}\cdot\text{CH}_2\text{Cl}_2$: C, 49.3; H, 4.3. Found: C, 49.6; H, 4.1. ^{31}P NMR (CDCl_3) δ 57.2 (s, 2P, P_1 and P_2); ^1H NMR (CDCl_3) δ 0.89 (t, 6H, $J_{\text{HH}} = 7.1$ Hz, $\text{COOCH}_2\text{CH}_3$), 3.82–3.86 (m, 4H, $\text{COOCH}_2\text{CH}_3$), 4.17 (d, 2H, $J_{\text{PH}} = 5.9$ Hz, PCHCOOEt), 7.51–7.94 (m, 20H, aromatics).

Liberation of (*R*, *R*)-diethyl-1,2-bis-(diphenylphosphino)-ethanedicarboxylate, (*R*, *R*)-84. A solution of (*R*, *R*)-90 (0.094 g) in CH₂Cl₂ (20 mL) was stirred vigorously with a saturated aqueous solution of KCN (1.000 g) for 2 h. The colorless organic layer was separated, washed with water (3 × 20 mL), and dried (MgSO₄). Upon the removal of solvent, a white solid was obtained: 0.060g (95% yield); [α]_D -275 (c 0.6, CHCl₃). ³¹P NMR (CDCl₃) δ -6.4 (s, 2P, P₁ and P₂); ¹H NMR (CDCl₃) δ 0.75 (t, 6H, $J_{\text{HH}} = 7.0$ Hz, COOCH₂CH₃), 3.39-3.43 (m, 4H, COOCH₂CH₃), 3.80 (t, 2H, $J_{\text{PH}} = 4.0$ Hz, PCHCOOEt), 7.15–7.62 (m, 20H, aromatics).

X-ray Crystal Structure Determinations of Complexes (*S*)-85 and (*R*, *R*)-90. Diffraction data were collected at the Nanyang Technological University using a Bruker X8 Apex diffractometer with Mo K α radiation (graphite monochromator). All non-H atoms were refined anisotropically, while Hydrogen atoms were introduced at a fixed distance from the Carbon atoms and were assigned fixed thermal parameters. The absolute configurations of the chiral complexes were determined unambiguously using the Flack parameter.¹¹⁰

Chapter 3

Asymmetric Synthesis of 1,2-Bis(diphenylphosphino)-1-Phenylethane *via* A Chiral Palladium Template Promoted Hydrophosphination Reaction

3.1 Introduction

Diphosphines with one chiral carbon center have been shown to be effective ligands in asymmetric hydrogenation of prochiral olefins.³² It has been demonstrated that a single chiral center may control the stereochemistry of these catalytical reactions when the phosphine coordinates with metal to form a rigid five-membered chelate ring.³³ 1,2-Bis(diphenylphosphino)-1-phenylethane (Phenphos) is such a chiral ditertiary phosphine. It was first synthesized from chiral Mandelic Acid *via* a 3-step transformation by King and Brown independently in 1978 and 1979 respectively.³⁶ However, no improved synthetic approach was reported to date. An attractive objective is the development of universal methods for the synthesis of such useful chiral phosphines from non-chiral starting materials. Our group have previously reported a series of chiral palladium template assisted asymmetric 1,2-addition reactions with alkynes or alkenes in the absence of a base promoter.⁸²⁻⁸⁴ It has been reported that external bases play an important role in some reactions, such as changing the addition pathways.¹¹¹ In this chapter we present the preparation of chiral PhenPhos by chiral metal template promoted asymmetric hydrophosphination reaction between diphenylphosphine and (*E*) or

(*Z*)-diphenylphosphinostyrene⁶⁴ with triethylamine as external base will be described.

3.2 Results and Discussion

In the absence of a metal ion, diphenylphosphine shows no reactivity with (*E*)- or (*Z*)-diphenylphosphinostyrene under ambient conditions. As illustrated in Scheme 3.1, the (*E*)- or (*Z*)-diphenylphosphinostyrene were coordinated to (*S*)-**72** regioselectively to form complexes **91a** and **91b** as solid powders in 99% isolated yields. The ³¹P NMR spectrum in CDCl₃ exhibited one single peak at δ 33.3 and 23.7 respectively for each coordination product. Complex **91a** could not be crystallized from the reaction solution while **91b** was crystallized from dichloromethane-hexane as yellow prisms (81% yield), $[\alpha]_D +36.7$ (*c* 0.3, CH₂Cl₂). The molecular structure and the coordination chemistry of **91b** were determined by X-ray crystallography (Fig. 3.1). Selected bond lengths and angles are given in Table 3.1.

Figure 3.1. Molecular structure and absolute stereochemistry of complex **91b**.

Table 3.1. Selected Bond Lengths (Å) and Bond Angles (deg) of **91b**

Pd(1)-P(1)	2.2617(6)
Pd(1)-Cl(1)	2.4047(6)
Pd(1)-N(1)	2.1283(19)
Pd(1)-C(1)	2.014(2)
P(1)-C(15)	1.810(2)
C(15)-C(16)	1.338(3)
N(1)-C(11)	1.510(3)
C(11)-C(10)	1.506(3)
C(10)-C(1)	1.384(3)
P(1)-Pd(1)-Cl(1)	93.90(2)
P(1)-Pd(1)- N(1)	174.74(5)
P(1)-Pd(1)- C(1)	93.78(6)
C(1)-Pd(1)-Cl(1)	164.92(6)
Cl(1)-Pd(1)-N(1)	91.36(5)
C(1)-Pd(1)-N(1)	81.05(8)
P(1)-C(15)-C(16)	128.96(17)
C(15)-C(16)-C(17)	130.83(19)

Addition of stoichiometric quantities of aqueous silver perchlorate to the dichloromethane solution containing the chloro complexes **91a,b** yielded the intermediate perchlorato complexes **92a,b** respectively. Complexes **92a** and **92b** were used for hydrophosphination reaction separately. They were not isolated from their corresponding previous reaction mixtures but were subsequently treated with diphenylphosphine separately at -78 °C in the presence of 50% equivalent of triethylamine to give the desired hydrophosphination products, **93a-d** in 12 h (Scheme 3.1). It is noteworthy that the hydrophosphination reactions did not occur without triethylamine as external base, even in the presence of the chiral amine

template. In addition, the reactions were highly regioselective, as the diphenylphosphino groups were added to the β -carbon of the diphenylphosphinostyrene to form five-membered chelate rings exclusively.^{82-84,}

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Upon treatment of diphenylphosphine with **92a**, three products were formed exhibiting three pairs of doublets in the crude ^{31}P NMR spectrum in the ratio 12:2:1: δ 48.2, 50.5 ($J_{\text{PP}} = 36.3$ Hz) for **93a**, 46.5, 50.1 ($J_{\text{PP}} = 36.6$ Hz) for **93b** and 25.1, 67.9 ($J_{\text{PP}} = 37.4$ Hz) for **93c**. Similarly, upon treatment of diphenylphosphine with **92b**, the reaction gave a 6:1 mixture of diastereomers **93a** and **93b**, along with trace amounts of **93c** and **93d** (δ 25.9 and 66.6 ($J_{\text{PP}} = 37.6$ Hz)). Unfortunately, the major product **93a** could not be isolated efficiently by chromatography or fractional crystallization. The two diastereomers **93a** and **93b** always co-crystallized together as a mixture. The mixture of **93a** and **93b** could be obtained from dichloromethane-hexane with the ratio of 6:1 as yellow crystals. The minor diastereomers, **93c** and **93d**, were not present in this crystallized material. The diastereomeric mixture **93a** and **93b** was subsequently redissolved in dichloromethane and fractional crystallization was attempted. A 1:1 mixture of **93a** and **93b** co-crystallized as yellow prisms from dichloromethane-diethyl ether and its X-ray structure was determined. Selected bond lengths and angles are given in Table 3.2 and Table 3.3.

The optically pure complex **93a** was left in the mother liquid. The X-ray crystallography affirms that two independent molecules are present in one asymmetric unit. The two molecules not only differ in relative bond lengths and

angles but also in the absolute configuration of the chiral carbon centers (C_{16} and C_{62}). The molecular structure of complex **93a** is given in Figure 3.2, which has an *R* absolute configuration at the newly formed chiral carbon centre C_{16} and the molecular structure of complex **93b** is given in Figure 3.3, which has an *S* absolute configuration at the newly formed chiral carbon centre C_{62} . The geometry at Pd_1 in complex **93a** is slightly distorted square plane with a distortion angle of 2.0° and a mean deviation from planarity of $0.013 \text{ \AA}$; the newly formed five-membered ring is found to adopt the λ ring conformation. On the other hand, the geometry at Pd_2 in complex **93b** exhibits a significantly distorted square plane with a distortion angle of 13.2° and a mean deviation from planarity of $0.165 \text{ \AA}$; the newly formed five-membered ring is found to adopt δ ring conformation. Based on the X-ray crystallography studies, complex **93b** is adopting a sterically unfavored δ ring conformation as it shows a significant distortion angle at the palladium(II) centre and significant deviation from the planarity.

Figure 3.2. Molecular structure and absolute stereochemistry of complex **93a**.

Table 3.2. Selected Bond Lengths (Å) and Bond Angles (deg) of **93a**

Pd(1)-C(1)	2.073(3)
Pd(1)-P(1)	2.3587(7)
Pd(1)-N(1)	2.146(3)
Pd(1)-P(2)	2.2442(8)
P(1)-C(16)	1.863(3)
P(2)-C(15)	1.842(3)
C(1)-Pd(1)-N(1)	80.19(12)

N(1)-Pd(1)-P(2)	175.28(8)
N(1)-Pd(1)-P(1)	100.17(8)
C(1)-Pd(1)-P(2)	95.12(9)
C(1)-Pd(1)-P(1)	177.98(10)
P(1)-Pd(1)-P(2)	84.50(3)
P(1)-C(16)-C(15)	104.47(19)
P(2)-C(15)-C(16)	110.3(2)

Figure 3.3. Molecular structure and absolute stereochemistry of complex **93b**.

Table 3.3. Selected Bond Lengths (Å) and Bond Angles (deg) of **93b**

Pd(2)-C(47)	2.065(3)
Pd(2)-P(4)	2.2358(8)
Pd(2)-N(2)	2.136(3)
Pd(2)-P(3)	2.3684(8)

P(3)-C(62)	1.871(4)
P(4)-C(61)	1.839(4)
C(47)-Pd(2)-N(2)	80.05(12)
N(2)-Pd(2)-P(4)	170.19(9)
N(2)-Pd(2)-P(3)	101.24(8)
C(47)-Pd(2)-P(4)	95.39(9)
C(47)-Pd(2)-P(3)	170.87(10)
P(4)-Pd(2)-P(3)	84.65(3)
P(3)-C(62)-C(61)	105.5(2)
P(4)-C(61)-C(62)	110.6(3)

The pure complex **93a** was obtained from the mother liquid after removal of 1:1 cocrystallized **93a** and **93b** completely. As illustrated in Scheme 3.2, conc. HCl was added subsequently to remove the chiral naphthylamine auxiliary resulting in the optically active dichloro complex (*R*)-**94** as yellow prisms (90% yield) from dichloromethane-diethyl ether: $[\alpha]_D +113$ (*c* 0.3, CH₂Cl₂). The ³¹P NMR spectrum of (*R*)-**94** in CDCl₃ exhibited two doublets at δ 43.0, 74.0 ($J_{PP} = 2.6$ Hz). The molecular structure and the absolute stereochemistry of (*R*)-**94** were determined by X-ray crystallography (Fig. 3.4). Selected bond lengths and angles are given in Table 3.4.

Figure 3.4. Molecular structure and absolute stereochemistry of complex (*R*)-94.

Table 3.4. Selected Bond Lengths (Å) and Bond Angles (deg) of (*R*)-94

Pd(1)-P(2)	2.2346(9)
Pd(1)-P(1)	2.2474(9)
Pd(1)-Cl(1)	2.3693(10)
Pd(1)-Cl(2)	2.3540(9)
P(1)-C(13)	1.836(3)
P(2)-C(14)	1.874(3)
C(13)-C(14)	1.536(4)
C(14)-C(15)	1.522(4)
P(2)-Pd(1)-P(1)	85.81(3)

P(2)-Pd(1)-Cl(1)	175.31(4)
P(1)-Pd(1)-Cl(1)	95.34(3)
P(2)-Pd(1)-Cl(2)	86.56(4)
P(1)-Pd(1)-Cl(2)	170.09(3)
Cl(1)-Pd(1)-Cl(2)	92.77(4)
P(2)-C(14)-C(13)	105.16(19)
P(1)-C(13)-C(14)	109.1(2)

The five-membered chelate ring has the asymmetric skew conformation of λ helicity with the phenyl substituent on the new formed carbon centre of *R* absolute configuration occupying an equatorial position. Aqueous potassium cyanide was added to a dichloromethane solution of (*R*)-**94**. After stirring vigorously for 1h, the colorless organic layer was separated, washed with water and dried (MgSO₄). Upon the removal of solvent, a white solid (*R*)-(-)-Phenphos^{36a} was obtained in 95% yield. The ³¹P NMR spectrum of the free ligand (*R*)-(-)-Phenphos in CDCl₃ exhibited two doublets at δ -21.2, 3.6 (J_{PP} = 17.4 Hz).

Scheme 3.2

To establish the identities of the two minor products **93c** and **93d**, the liberated optically pure (*R*)-(-)-Phenphos was recombined to (*S*)-**79** as illustrated in Scheme 3.3. The ³¹P NMR spectrum (CDCl₃) of the crude product exhibited only two pairs of doubles at δ 48.2, 50.5 (J_{PP} = 36.3 Hz) and 25.1, 67.9 (J_{PP} = 37.4 Hz). These signals are identical to those recorded for **93a** and **94c** generated in the

original hydrophosphination reaction. The ^{31}P NMR spectrum (CDCl_3) of the crude recomplexation mixture from (*R*)-(-)-Phenphos and (*R*)-**79** exhibited two pairs of doubles at δ 46.5, 50.1 ($J_{\text{PP}} = 36.6$ Hz) and 25.9, 66.6 ($J_{\text{PP}} = 37.6$ Hz). These signals were identical with those observed for **93b** and **93d**. Complexes **93b** and **95**, **93d** and **96** are thus two pairs of enantiomers. As expected, the enantiomeric complexes exhibited the same NMR chemical signals. Thus, the NMR studies confirmed that diastereomer **93d** was indeed a minor product of the asymmetric synthesis.

In general, (*E*)- and (*Z*)-diphenylphosphinostyrene generated the hydrophosphination products **93a** and **93b** with the same ratio of 6:1, which is not in agreement with what we observed in our previous experiments of hydrophosphination reactions.⁸² In the previous studies, *trans* and *cis* coordinated alkenes did not yield major products with same chirality. However, this can be explained by consideration of the possible reaction pathways as illustrated in Scheme 3.4. In principle, the transition state A and B are electronically more

favorable than other possible pathways. The π -accepting styrenylphosphine is coordinated in the position *trans* to the σ -donating NMe group, while the electron-rich phosphido moiety is located *trans* to the strong π -accepting ortho-metalated carbon atom.⁹¹ With pathway A, the (*E*)-isomer **92a** would generate complex **93a** as the major product, in which the new stereogenic carbon center adopts the *R* absolute configuration. In this transition state, severe interchelate repulsions between the chiral auxiliary and the reacting phosphorus substrates are absent. With pathway B, the (*E*)-isomer **92a** would generate complex **93b** as minor product due to the influence of the interchelate repulsions by which the new stereogenic carbon center adopts the *S* absolute configuration. However, with pathway A, the (*Z*)-isomer **92b** would only generate complex **93b** as minor product because of the severe interchelate repulsions between the chiral auxiliary and phenyl substrate present in **92b**.

Scheme 3.4

For this reason, the (Z)-isomer **92b** would prefer generation of complex **93a** as major product through pathway B. It is noteworthy that complex **93a** which was generated from **92b** through pathway B adopted a δ ring conformation initially. It would however transfer to a more stable λ ring conformation in solution easily. From the discussions above, we believe that (E)- and (Z)-diphenylphosphinostyrene both generate complex **93a** as major product but through different pathways.

3.3 Conclusion

In conclusion, the synthesis of chiral diphosphine *via* chiral amine template assisted asymmetric hydrophosphination has been demonstrated. Triethylamine is essential to this reaction as it play the role as external base. The reactions proceeded with high regio- and stereoselectivities, generating chiral PhenPhos with high yield.

3.4 Experimental Section

Reactions involving air-sensitive compounds were performed under a positive pressure of purified 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 0.1dm cell at 25 °C with a Perkin-Elmer model 341 polarimeter. Elemental analyses were performed by the staff in the Elemental Analysis Laboratory of the Division of Chemical and Biological Chemistry of Nanyang

Technological University. Melting points were measured using the SRS Optimeit Automated Melting Point System, SRS MPA100.

All solvents used for the 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(acetonitrile) bis(acetonitrile)[(*S*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-*C, N*]-palladium(II) perchlorate ((*R*)-72) were prepared according to literature methods.^{25c} Tertiary phosphine (*E*) or (*Z*)-diphenylphosphinostyrene were prepared according to literature methods.⁶⁴

[(*S*)-Chloro[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C, N*]][(*E*)-Diphenylphosphinostyrene -*P*]palladium(II), 91a. A mixture of (*S*)-1 (0.590 g) and (*Z*)-diphenylphosphinostyrene (0.501 g) was stirred in dichloromethane (50 mL) at room temperature for 2 h. The solvent was removed and complex 91a was obtained as yellow powder, 1.090 g (99% yield). $[\alpha]_D +75.6$ (*c* 0.2, CH₂Cl₂); Mp 120-121 °C (dec); Anal. Calcd. for C₃₄H₃₃ClNPPd: C, 65.0; H, 5.3; N, 2.2. Found: C, 64.7; H, 5.4; N, 2.2. ³¹P NMR (CDCl₃) δ 33.3; ¹H NMR (CDCl₃) δ 2.09 (d, 3H, CHMe, ³*J*_{HH} = 6.2 Hz), 2.82 (s, 3H, NMe_{eq}), 3.03 (d, 3H, ⁴*J*_{PH} = 3.3 Hz, NMe_{ax}), 4.41 (qn, 1H, ³*J*_{HH} = ⁴*J*_{PH} = 6.2 Hz, CHMe), 6.61 (dd, 1H, ²*J*_{PH} = 17.6 Hz, ³*J*_{HH} = 8.8 Hz, PCH), 6.76 (dd, 1H, ³*J*_{PH} = 6.1 Hz, ³*J*_{HH} = 8.8 Hz, PCCH), 6.79-8.07 (m, 21H, aromatics).

[(*S*)-Chloro[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C, N*]][(*Z*)-Diphenylphosphinostyrene -*P*]palladium(II), 91b. A mixture of (*R*)-72 (0.594 g) and (*Z*)-

diphenylphosphinostyrene (0.504 g) was stirred in dichloromethane (50 mL) at room temperature for 2 h. The solvent was removed and complex 91b was obtained from dichloromethane and diethyl ether as yellow crystals, 0.889 g (81% yield). $[\alpha]_D +36.7$ (c 0.3, CH_2Cl_2); Mp 183-184 °C (dec); Anal. Calcd. for $\text{C}_{34}\text{H}_{33}\text{ClNPPd}$: C, 65.0; H, 5.3; N, 2.2. Found: C, 64.7; H, 5.4; N, 2.2. ^{31}P NMR (CDCl_3) δ 23.7; ^1H NMR (CDCl_3) δ 1.80 (d, 3H, CHMe , $^3J_{\text{HH}} = 6.2$ Hz), 2.58 (d, 3H, $^4J_{\text{PH}} = 1.2$ Hz, NMe_{eq}), 2.94 (d, 3H, $^4J_{\text{PH}} = 3.3$ Hz, NMe_{ax}), 4.29 (qn, 1H, $^3J_{\text{HH}} = ^4J_{\text{PH}} = 6.2$ Hz, CHMe), 6.72 (dd, 1H, $^2J_{\text{PH}} = 13.1$ Hz, $^3J_{\text{HH}} = 6.6$ Hz, PCH), 6.84 (dd, 1H, $^3J_{\text{PH}} = 8.6$ Hz, $^3J_{\text{HH}} = 6.6$ Hz, PCCH), 7.03-7.87 (m, 21H, aromatics).

Hydrophosphination of [(*S*)-Chloro[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*][(*E/Z*)-Diphenyl-phosphinostyrene -*P*]palladium(II), 91a/b. Complex **91a/b** (0.582 g) in dichloromethane (100 mL) and aqueous silver perchlorate (0.400 g) were stirred vigorously at room temperature for 2 h. The mixture was filtered through Celite, washed with water (3 X 30 mL) and dried with MgSO_4 . The mixture was then degassed and treated with diphenylphosphine (0.172 g) and triethylamine (0.047 g) at -78 °C for 12 h. The crude product was recrystallized from dichloromethane and diethyl ether to give the 1:1 mixture of **93a,b** as yellow crystals, 0.228 g (28% yield). $[\alpha]_D +48.4$ (c 0.6, CH_2Cl_2); Mp 235°C (dec); Anal. Calcd for $\text{C}_{46}\text{H}_{44}\text{ClNO}_4\text{P}_2\text{Pd}$: C, 62.9; H, 5.1; N, 1.6. Found: C, 62.4; H, 5.2; N, 1.6. Spectroscopic assignments follow. [(*S*)-chloro[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*][(*R*)-1,2-bis(diphenyl phosphino)-1-phenylethane-*P*¹, *P*²] palladium(II) Perchlorate, **93a**: ^{31}P NMR (CDCl_3) δ 48.2,

50.5 ($J_{PP} = 36$ Hz); ^1H NMR (CDCl_3) δ 1.98 (d, 3H, CHMe , $^3J_{HH} = 6.2$ Hz), 2.40 (s, 3H, NMeeq), 2.58 (s, 3H, NMeax), 2.62-3.25 (m, 2H, PCH_2), 3.51-3.65 (m, 1H, PCH), 4.55 (qn, 1H, $^3J_{HH} = ^4J_{PH} = 6.2$ Hz, CHMe), 6.36-8.35 (m, 31H, aromatics). [(*S*)-chloro[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*][(*S*)-1,2-bis(diphenyl phosphino)-1-phenylethane- P^1 , P^2]palladium(II) Perchlorate **93b**: ^{31}P NMR (CDCl_3) δ 46.5, 50.1 ($J_{PP} = 37$ Hz), ^1H NMR (CDCl_3) δ 1.64 (d, 3H, CHMe , $^3J_{HH} = 6.2$ Hz), 2.24 (s, 3H, NMeeq), 2.62-3.25 (m, 2H, PCH_2), 2.96 (s, 3H, NMeax), 3.51-3.65 (m, 1H, PCH), 4.44 (qn, 1H, $^3J_{HH} = ^4J_{PH} = 6.2$ Hz, CHMe), 6.36-8.35 (m, 31H, aromatics).

(*R*)-Dichloro[1,2-bis(diphenylphosphino)-1-phenylethane- P^1 , P^2] palladium (II), (*R*)-94. Concentrated HCl (10 mL) was added to a solution of **93a** (0.200 g) in dichloromethane (30 mL). The reaction mixture was stirred vigorously at room temperature for 12 h, washed with water (3 X 20 mL), and dried (MgSO_4). Crystallization of the crude product from dichloromethane and diethyl ether gave the dichloro complex as yellow crystals, 0.150 g (90% yield). $[\alpha]_D +113$ (c 0.3, CH_2Cl_2); Mp: 210°C (dec); Anal.Calcd for $\text{C}_{33}\text{H}_{30}\text{Cl}_4\text{P}_2\text{Pd}$: C53.8; H4.1. Found: C53.5; H4.3. ^{31}P NMR (CDCl_3) δ 43.0, 74.0 ($J_{PP} = 2.6$ Hz); ^1H NMR (CDCl_3) δ 2.70-2.97 (m, 2H, PCH_2CHPh), 3.93-4.00 (m, 1H, PCHPh), 6.55-8.29 (m, 25H, aromatics).

Liberation of (*R*)-1,2-bis(diphenylphosphino)-1-phenylethane, (*R*)-(-)-Phenphos. A solution of (*R*)-94 (0.066 g) in dichloromethane was stirred

vigorously with a saturated aqueous solution of potassium cyanide (1.00 g) for 2 h. The organic layer was separated, washed with water (3 X 20 mL), and dried (MgSO_4). Upon removal of solvent, a white solid was obtained: 0.050 g (95% yield). ^{31}P NMR (CDCl_3) δ -21.2, 3.6 ($J_{\text{PP}} = 17.4$ Hz).

X-ray Crystal Structure Determinations of Complexes 91b, 93a, 93b and (*R*)-94. Diffraction data were collected at the Nanyang Technological University using a Bruker X8 Apex diffractometer with Mo $K\alpha$ radiation (graphite monochromator). All non-H atoms were refined anisotropically, while Hydrogen atoms were introduced at a fixed distance from the Carbon atoms and were assigned fixed thermal parameters. The absolute configurations of the chiral complexes were determined unambiguously using the Flack parameter.¹¹⁰

Chapter 4

Asymmetric Synthesis of Diphosphine Ligands Containing Phosphorus and Carbon Stereogenic Centers by Means of A Chiral Palladium Complex Promoted Hydrophosphination Reaction

4.1 Introduction

The early development of optically active P-chiral phosphorus ligands for chiral metal catalysts can be attributed to the studies of homogeneous asymmetric hydrogenation initiated by Knowles¹⁴ and Horner¹⁵ in the late 1960s. Although the first P-chiral diphosphine DIPAMP has proven to be a very efficient hydrogenation ligand, the development of new P-chiral diphosphines continues to pose considerable challenges.¹¹² Diphosphines with chiral carbon center(s) at backbones, such as Kagan's DIOP²¹ and Bosnich's ChiraPhos²³ are another group of effective phosphine ligands in asymmetric synthesis. Their pioneering research showed that not only do P-chiral phosphorus ligands have the capability to achieve high enantioselectivity; phosphine ligands with backbone chirality could also provide excellent catalytic effects.¹⁸ However, diphosphines which possess these two types of stereogenic centers in the same framework are less studied.¹¹³ Clearly these would be interesting chiral ligands and deserve further examination of their catalytic properties.

Our group had previously reported a series of chiral palladium template assisted asymmetric hydrophosphination reactions to synthesis optically pure phosphines with their backbone chirality.^{82-84, 111} In pursuing the interest in the synthesis of P-stereogenic diphosphines with selected functionalities, this chapter describes the preparation of chiral diphosphines which contain both phosphorus and carbon stereogenic centers by chiral metal template promoted asymmetric hydrophosphination reaction between diphenylphosphine and phenyldi[(*Z*)-prop-1-enyl]phosphine.

4.2 Results and Discussion

In the absence of a metal ion, diphenylphosphine shows no reactivity with phenyldi[(*Z*)-prop-1-enyl]phosphine under ambient conditions. As illustrated in Scheme 4.1, phenyldi[(*Z*)-prop-1-enyl]phosphine was coordinated to (*R*)-**72** regioselectively to form the neutral complex (*R*)-**97**. Upon abstraction of the chloro ligand in (*R*)-**97** with silver perchlorate gave the perchlorato complex (*R*)-**98**. Complex (*R*)-**98** was not isolated and was treated directly with one equivalent of diphenylphosphine at -78 °C to give the hydrophosphination products, **99a** and **99b**. Prior to purification, the ³¹P NMR spectrum in CDCl₃ exhibited two pairs of doublets in the ratio of 1:1: δ 33.6, 49.9 (J_{PP} = 26.1 Hz) for **99a** and 29.8, 49.0 (J_{PP} = 29.0 Hz) for **99b**. It is noteworthy that only one of the two vinyl groups in complex (*R*)-**3** reacted with diphenylphosphine and thus made the newly formed five membered diphosphine chelates each had one phosphorus and one carbon stereogenic center. Both the diphosphine chelates formed in **99a** and **99b** adopt the

same *R* absolute configuration at the newly generated carbon chiral centers. It needs to be noted that **99a** and **99b** are two of the eight possible stereoisomeric products of the hydrophosphination reaction. No other products were detected by ^{31}P NMR spectroscopy in the crude solution.

Scheme 4.1

The hydrophosphination reaction was highly regioselective, as the diphenylphosphino group was added to the β -carbon of the phenyldi[(*Z*)-prop-1-enyl]phosphine to form the stereoisomeric five membered chelate rings exclusively. In addition, the newly generated stereogenic phosphorus centers were occupying the coordination sites *trans* to the NMe₂ group of the chiral metal template. It is well-known that the chloro ligand in complex (*R*)-**97** is kinetically and thermodynamically stable. In order to provide a vacant coordination site for the reacting diphenylphosphine, (*R*)-**97** was treated with silver perchlorate prior to the introduction of diphenylphosphine into the reaction mixture.¹¹⁴

The two diastereomeric products could be separated into their stereoisomerically pure forms by fractional crystallization. Complex **99a** was isolated as colorless crystals from chloroform and diethyl ether in 35% yield, [α]_D -151 (*c* 0.5, CH₃Cl). The molecular structure and the absolute stereochemistry of **99a** were determined by X-ray crystallography (Figure 4.1) Selected bond lengths and angles of **99a** are listed in Table 4.1. Complex **99b** was subsequently obtained from acetonitrile and diethyl ether as colorless crystals in 42% yield, [α]_D +84 (*c* 1.0, CH₂Cl₂).

Complexes **99a,c** and **99b,d** are four of the eight possible stereoisomeric products of the hydrophosphination reaction. Complexes **99a,c** are *cis-trans* regioisomers which adopt the same *R* absolute configuration at the newly generated stereogenic carbon centers and *S* absolute configuration at the newly generated chiral phosphorus centers within the diphosphine chelates but differ in the relative regio arrangement of the four nonequivalent donor atoms on the metal templates. Similarly, **99b,d** are regioisomers with *R* absolute configuration at the newly

generated stereogenic carbon centers and *R* absolute configuration at the newly generated chiral phosphorus centers.

Figure 4.1. Molecular structure and absolute stereochemistry of complex **99a**.

Table 4.1. Selected Bond Lengths (Å) and Angles (deg) for **99a**

Pd(1)-P(1)	2.3680(7)
Pd(1)-P(2)	2.2473(7)
Pd(1)-N(1)	2.153(2)
Pd(1)-C(1)	2.058(3)
P(1)-C(28)	1.847(3)
P(2)-C(29)	1.849(3)
C(28)-C(29)	1.535(4)

C(1)-Pd(1)-N(1)	80.38(9)
N(1)-Pd(1)-P(1)	101.15(6)
P(1)-Pd(1)-P(2)	84.57(3)
P(2)-Pd(1)-C(1)	94.06(7)
N(1)-Pd(1)-P(2)	173.50(6)
C(1)-Pd(1)-P(1)	176.88(8)
Pd(1)-P(1)-C(28)	106.22(9)
Pd(1)-P(2)-C(29)	108.59(10)
P(1)-C(28)-C(29)	104.8(2)
P(2)-C(29)-C(28)	111.63(19)

The coordinated ligand phenyldi[(*Z*)-prop-1-enyl]phosphine in complex (*R*)-**98** has two vinylic double bonds. However, when two equivalent of diphenylphosphine was used, no other products besides **99a** and **99b** were detected by ^{31}P NMR spectroscopy under similar reaction condition. One unreacted carbon-carbon double bond remained in each complex **99a** and **99b**. It is believed that the first diphenylphosphine molecule coordinates to complex (*R*)-**98** before the intramolecular hydrophosphination reaction takes place. The intermolecular hydrophosphination reaction between phenyldi[(*Z*)-prop-1-enyl]-phosphine molecule and the second diphenylphosphine molecule is not occurring or is extremely slow compared to the intramolecular one.

When complex **99a** or **99b** was kept at room temperature in dichloromethane for several days, equilibrium mixtures of regioisomers were formed. When a solution of **99a** was monitored by ^{31}P NMR spectrum, a new pair of doublets at δ 22.3, 75.3 ($J_{\text{PP}} = 21.1$ Hz) was detected, which was assigned to **99c**.⁸² In the same way, **99d** was assigned as **99b**'s regioisomer: the ^{31}P NMR spectrum in CDCl_3 exhibited a

new pair of doublets at δ 15.9, 76.4 ($J_{\text{PP}} = 22.1$ Hz). Upon slow recrystallization, the *cis-trans* regioisomers **99b** and **99d** cocrystallized in equal quantities as colorless crystals from acetonitrile and diethyl ether in 90% yield, $[\alpha]_{\text{D}} -20$ (c 0.3, CHCl_3). A crystallographic analysis revealed that two regioisomers, **99b,d** were indeed present in the same unit cell (Figure 4.2 and 4.3). Selected bond lengths and angles of **99b** and **99d** are listed in Table 4.2 and Table 4.3 respectively. As expected, the five-membered diphosphine chelates were formed in these stereoisomers. The newly formed stereogenic carbon centers in complexes **99a**, **99b** and **99d** all adopt the *R* absolute configuration.

Figure 4.2. Molecular structure and absolute stereochemistry of complex **99b**.

Table 4.2. Selected Bond Lengths (Å) and Angles (deg) for **99b**

Pd(2)-P(3)	2.366(3)
Pd(2)-P(4)	2.242(3)
Pd(2)-N(2)	2.135(10)
Pd(2)-C(39)	2.089(10)
P(3)-C(63)	1.869(13)
P(4)-C(62)	1.820(11)
C(63)-C(62)	1.535(14)
C(39)-Pd(2)-N(2)	78.9(4)
N(2)-Pd(2)-P(3)	103.3(3)
P(3)-Pd(2)-P(4)	84.97(11)
P(4)-Pd(2)-C(39)	93.6(3)
N(2)-Pd(2)-P(4)	170.9(3)
C(39)-Pd(2)-P(3)	169.6(3)
Pd(2)-P(3)-C(63)	104.2(3)
Pd(2)-P(4)-C(62)	109.4(4)
P(3)-C(63)-C(62)	105.4(8)
P(4)-C(62)-C(63)	111.5(7)

Table 4.3. Selected Bond Lengths (Å) and Angles (deg) for **99d**

Pd(1)-P(1)	2.348(3)
Pd(1)-P(2)	2.243(3)
Pd(1)-N(1)	2.136(8)
Pd(1)-C(10)	2.097(9)
P(1)-C(24)	1.848(12)
P(2)-C(25)	1.866(13)
C(24)-C(25)	1.525(17)
C(10)-Pd(1)-N(1)	80.2(4)
N(1)-Pd(1)-P(1)	99.1(2)

P(1)-Pd(1)-P(2)	84.35(10)
P(2)-Pd(1)-C(10)	96.0(3)
N(1)-Pd(1)-P(2)	172.6(2)
C(10)-Pd(1)-P(1)	176.4(3)
Pd(1)-P(1)-C(24)	106.4(4)
Pd(1)-P(2)-C(25)	109.9(4)
P(1)-C(24)-C(25)	111.6(8)
P(2)-C(25)-C(24)	104.7(9)

Figure 3. Molecular structure and absolute stereochemistry of complex **99d**.

As shown in Scheme 4.2, the (*R*)-naphthylamine auxiliary can be chemoselectively removed from **99a** by treatment with concentrated hydrochloric acid to give the dichloride **100a** as yellowish crystals from acetonitrile and diethyl ether in 88% isolated yield, $[\alpha]_D -88$ (*c* 0.6, CH₂Cl₂). The ³¹P NMR spectrum of the dichloro complex in CDCl₃ showed a pair of doublets: δ 42.6, 75.2 ($J_{PP} = 6.3$ Hz). Treatment of a dichloromethane solution of **100a** with aqueous potassium cyanide for 30 min liberated the optically pure diphosphine **101a** as a white solid in quantitative yield, $[\alpha]_{546} +70$ (*c* 0.5, CHCl₃). The ³¹P NMR spectrum of the free diphosphine **101a** in CDCl₃ showed a pair of doublets: δ -44.8, 2.0 ($J_{PP} = 20.8$ Hz).

Scheme 4.2

Similarly, **99b,d** were treated with concentrated hydrochloric acid to remove the chiral amine auxiliary chemoselectively (Scheme 4.3). The ³¹P NMR spectrum of the dichloro complex in CDCl₃ showed a pair of doublets: δ 39.7, 71.2 ($J_{PP} = 5.6$ Hz). The neutral dichloro complex **100b** crystallized from acetonitrile and diethyl ether as yellowish crystals in its optically pure form, $[\alpha]_D -60$ (*c* 0.5, CH₂Cl₂). Subsequently, the dichloro complex **100b** underwent ligand displacement with aqueous potassium cyanide at room temperature to generate **101b** in its optically pure form in 95% yield, $[\alpha]_D +246$ (*c* 0.5, CHCl₃). The ³¹P NMR spectrum of the free ligand in CDCl₃ showed a pair of doublets: δ -46.5, 2.0 ($J_{PP} = 20.5$ Hz).

Scheme 4.3

In order to confirm the optical purity of the free diphosphines, the liberated optically pure **101a** was recoordinated to (*R*)-**79** (Scheme 4.4). The ^{31}P NMR spectrum (CDCl_3) of the crude product exhibited only two pairs of doubles at δ 33.6, 49.9 ($J_{\text{PP}} = 26.1$ Hz) and 22.3, 75.3 ($J_{\text{PP}} = 21.1$ Hz). These signals are identical to those recorded for **99a** and **99c**. The ^{31}P NMR spectrum (CDCl_3) of the crude recomplexation mixture from **101b** and (*R*)-**79** exhibited two pairs of doubles at δ 29.8, 49.0 ($J_{\text{PP}} = 29.0$ Hz) and 15.9, 76.4 ($J_{\text{PP}} = 22.1$ Hz). These signals were identical with those observed for **99b** and **99d**. The spectrum specific studies confirmed that diastereomer **99c** and **99d** were indeed regioisomers of **99a** and **99c** respectively and the liberated diphosphines **101a** and **101b** are therefore confirmed to be optically pure.

Scheme 4.4

In the absence of a metal ion, diphenylphosphine shows no reactivity with phenyldi[(*E*)-prop-1-enyl]phosphine under ambient conditions. As illustrated in Scheme 4.5, phenyldi[(*E*)-prop-1-enyl]phosphine was coordinated to (*R*)-**72** regioselectively to form the neutral complex (*R*)-**102**. Upon abstraction of the chloro ligand with silver perchlorate gave the perchlorato complex (*R*)-**103**. Complex (*R*)-**103** was not isolated but was treated directly with diphenylphosphine at -78 °C to give the hydrophosphination products, **104a**, **104b** and **104c**. Prior to purification, the ³¹P NMR spectrum in CDCl₃ exhibited three pairs of doublets in the ratio of 5:6:2: δ 47.1, 48.0 ($J_{\text{PP}} = 33$ Hz), 46.1, 47.0 ($J_{\text{PP}} = 35$ Hz), and 46.5, 48.8 ($J_{\text{PP}} = 31$ Hz) for **104a**, **104b** and **104c**, respectively.

The two diastereomeric products **104a** and **104c** could be separated into their stereoisomerically pure forms by fractional crystallization. Complex **104a** was isolated as colorless crystals from dichloromethane and diethyl ether in 30% yield, $[\alpha]_{\text{D}}^{25} -31$ (c 0.5, CH₃Cl). **104c** was obtained as colorless crystals in 13% yield, $[\alpha]_{\text{D}}^{25} -30$ (c 0.5, CH₃Cl). The molecular structure and the absolute stereochemistry of **104a** and **104c** were determined by X-ray crystallography (Figure 4.4 and 4.5).

Selected bond lengths and angles of **104a** and **104c** are listed in Table 4.4 and Table 4.5 respectively.

Scheme 4.5

Figure 4.4. Molecular structure and absolute stereochemistry of complex **104a**.

Table 4.4. Selected Bond Lengths (Å) and Angles (deg) for **104a**

Pd(1)-P(1)	2.3602(15)
Pd(1)-P(2)	2.2474(15)
Pd(1)-N(1)	2.135(5)
Pd(1)-C(1)	2.057(6)
P(1)-C(27)	1.842(7)
P(2)-C(29)	1.847(6)
C(27)-C(29)	1.569(10)
C(1)-Pd(1)-N(1)	80.3(2)
N(1)-Pd(1)-P(1)	99.72(13)
P(1)-Pd(1)-P(2)	84.95(6)
P(2)-Pd(1)-C(1)	95.02(16)
N(1)-Pd(1)-P(2)	175.26(13)
C(1)-Pd(1)-P(1)	176.80(16)
Pd(1)-P(1)-C(27)	105.0(2)
Pd(1)-P(2)-C(29)	108.8(2)
P(1)-C(27)-C(29)	105.3(4)
P(2)-C(29)-C(27)	107.9(5)

Figure 4.5. Molecular structure and absolute stereochemistry of complex **104c**.

Table 4.5. Selected Bond Lengths (Å) and Angles (deg) for **104c**

Pd(1)-P(1)	2.3746(18)
Pd(1)-P(2)	2.2771(16)
Pd(1)-N(1)	2.147(5)
Pd(1)-C(1)	2.083(7)
P(1)-C(28)	1.862(7)
P(2)-C(29)	1.849(9)
C(28)-C(29)	1.468(11)
C(1)-Pd(1)-N(1)	80.0(2)
N(1)-Pd(1)-P(1)	101.03(15)
P(1)-Pd(1)-P(2)	83.84(6)
P(2)-Pd(1)-C(1)	95.09(17)
N(1)-Pd(1)-P(2)	174.36(15)

C(1)-Pd(1)-P(1)	178.77(18)
Pd(1)-P(1)-C(28)	104.6(2)
Pd(1)-P(2)-C(29)	108.4(3)
P(1)-C(28)-C(29)	106.5(5)
P(2)-C(29)-C(28)	111.0(6)

As shown in Scheme 4.6, the (*R*)-naphthylamine auxiliary can be chemoselectively removed from **104a** by treatment with concentrated hydrochloric acid to give the dichloride **105a** as colorless crystals from dichloromethane and diethyl ether in 85% isolated yield. The ^{31}P NMR spectrum of the dichloro complex in CDCl_3 showed a pair of doublets: δ 49.0, 72.6 ($J_{\text{PP}} = 5.1$ Hz). Similarly, **104c** was treated with concentrated hydrochloric acid to remove chiral amine auxiliary chemoselectively. The ^{31}P NMR spectrum of the dichloro complex in CDCl_3 showed a pair of doublets: δ 49.0, 72.6 ($J_{\text{PP}} = 5.1$ Hz). The neutral dichloro complex **105c** crystallized from dichloromethane and diethyl ether as yellow prisms as its optically pure form. The molecular structure and the absolute stereochemistry of **105a** and **105c** were determined by X-ray crystallography (Figure 4.6 and 4.7). Selected bond lengths and angles of **105a** and **105c** are listed in Table 4.6 and Table 4.7 respectively.

The hydrophosphination reaction mother liquid apart from **104a** and **104c** was treated with concentrate hydrochloric acid and stirred vigorously overnight. The reaction mixture was washed with water and dried with magnesium sulfate and subsequently crystallized from dichloromethane and diethyl ether as colorless crystals. The ^{31}P NMR spectrum of the dichloro complex **105b** in CDCl_3 showed a pair of doublets: δ 48.4, 71.2 ($J_{\text{PP}} = 5.2$ Hz).

Scheme 4.6

Figure 4.6. Molecular structure and absolute stereochemistry of complex 105a.

Table 4.6. Selected Bond Lengths (Å) and Angles (deg) for **105a**

Pd(1)-P(1)	2.2318(8)
Pd(1)-P(2)	2.2240(8)
Pd(1)-Cl(1)	2.3638(8)
Pd(1)-Cl(2)	2.3698(8)
P(1)-C(14)	1.858(3)
P(2)-C(15)	1.833(4)
C(14)-C(15)	1.522(5)
Cl(2)-Pd(1)-Cl(1)	95.92(3)
Cl(1)-Pd(1)-P(1)	89.98(3)
P(1)-Pd(1)-P(2)	86.04(3)
P(2)-Pd(1)-Cl(2)	88.17(3)
Cl(1)-Pd(1)-P(2)	175.03(3)
Cl(2)-Pd(1)-P(1)	173.75(3)
Pd(1)-P(1)-C(14)	108.23(11)
Pd(1)-P(2)-C(15)	108.25(12)
P(1)-C(14)-C(15)	107.7(2)
P(2)-C(15)-C(14)	107.8(2)

Figure 4.7. Molecular structure and absolute stereochemistry of complex **105c**

Table 4.7. Selected Bond Lengths (Å) and Angles (deg) for **105c**

Pd(1)-P(1)	2.2372(9)
Pd(1)-P(2)	2.2512(9)
Pd(1)-Cl(1)	2.3476(9)
Pd(1)-Cl(2)	2.3630(9)
P(1)-C(14)	1.862(3)
P(2)-C(15)	1.830(3)
C(14)-C(15)	1.528(4)
Cl(2)-Pd(1)-Cl(1)	91.42(3)
Cl(1)-Pd(1)-P(1)	87.55(3)
P(1)-Pd(1)-P(2)	85.88(3)
P(2)-Pd(1)-Cl(2)	95.30(3)
Cl(1)-Pd(1)-P(2)	173.04(4)
Cl(2)-Pd(1)-P(1)	175.63(4)
Pd(1)-P(1)-C(14)	107.74(10)
Pd(1)-P(2)-C(15)	108.06(10)
P(1)-C(14)-C(15)	106.18(19)
P(2)-C(15)-C(14)	109.39(18)

4.3 Conclusion

In conclusion, an attractive synthesis of chiral diphosphines containing both phosphorus and carbon stereogenic centers *via* chiral organopalladium template promoted asymmetric hydrophosphination has been demonstrated. The hydrophosphination reaction proceeds with high regio- and stereoselectivity under mild conditions. Both carbon and phosphorous stereocenters can be generated efficiently in this reaction.

4.4 Experimental Section

Reactions involving air-sensitive compounds were performed under a positive pressure of purified 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 0.1dm cell at 25 °C with a Perkin-Elmer model 341 polarimeter. Elemental analyses were performed by the staff in the Elemental Analysis Laboratory of the Division of Chemical and Biological Chemistry of Nanyang Technological University. Melting points were measured using the SRS Optimize Automated Melting Point System, SRS MPA100.

All solvents used for the 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(acetonitrile) bis(acetonitrile)[(*S*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-*C*, *N*]-palladium(II) perchlorate ((*R*)-**72**) were prepared according to literature methods.^{25c} phenyldi[(*Z*)-prop-1-enyl]phosphine, complexes (*R*)-**97**, (*R*)-**98**, (*R*)-**102** and (*R*)-**103** were prepared as previously reported by our group.¹¹⁴

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

Hydrophosphination of complex (*R*)-98. Complex (*R*)-**97** (1.20 g) in dichloromethane (30 mL) and aqueous silver perchlorate (0.80 g) were stirred vigorously at room temperature for 2 h. The mixture was filtered through Celite (to

remove silver chloride), washed with water (3 X 30 mL), and dried (magnesium sulfate). The mixture was then degassed and treated with diphenylphosphine (0.35 g) at -78 °C for 12 h. By fractional crystallization, **99a** was isolated as colorless crystals from chloroform and diethyl ether: 0.56 g (35% yield). Mp 205-206 °C (dec); $[\alpha]_D -151$ (c 0.5, CH₃Cl). Anal.Calcd for C₃₈H₄₂ClNO₄P₂Pd: C, 58.5; H, 5.4; N, 1.8. Found: C, 58.4; H, 5.5; N, 1.8. ³¹P NMR (CDCl₃) δ 33.6, 49.9 ($J_{PP} = 26.1$ Hz); ¹H-NMR (CDCl₃) δ 0.96 (dd, 3H, $^3J_{PH} = 12.9$ Hz, $^3J_{HH} = 7.0$ Hz, P¹CHMe), 1.71 (d, 3H, $^3J_{HH} = 6.2$ Hz, CHMe), 2.01 (d, 3H, $^3J_{HH} = 5.9$ Hz, P²CCMe), 2.09-2.23 (m, 1H, P¹CHH'), 2.43 (s, 3H, NMeeq), 2.44-2.56 (m, 1H, P¹CHH'), 2.95 (s, 3H, NMeax), 2.96-3.11 (m, 1H, P¹CHMe), 4.51 (qn, 1H, $^3J_{HH} = ^4J_{PH} = 6.2$ Hz, CHMe), 6.36 (dd, 1H, $^3J_{PH} = ^3J_{HH} = 11.7$ Hz, P²CH), 6.70 (ddq, 1H, $^3J_{PH} = 38.8$ Hz, $^3J_{HH} = 11.7$ Hz, $^3J_{HH} = 7.0$ Hz, P²CCH), 7.02-8.18 (m, 21H, aromatics). **99b** was obtained from acetonitrile and diethyl ether as colorless crystals: 0.68 g (42% yield). Mp 194-196 °C (dec); $[\alpha]_D +84$ (c 1.0, CH₂Cl₂). Anal.Calcd for C₃₈H₄₂ClNO₄P₂Pd: C, 58.5; H, 5.4; N, 1.8. Found: C, 58.4; H, 5.5; N, 1.8. ³¹P NMR (CDCl₃) 29.8, 49.0 ($J_{PP} = 29.0$ Hz); ¹H-NMR (CDCl₃) δ 1.21 (dd, 3H, $^3J_{PH} = 12.1$ Hz, $^3J_{HH} = 6.9$ Hz, P¹CHMe), 1.71 (d, 3H, $^3J_{HH} = 6.2$ Hz, CHMe), 1.94-2.20 (m, 2H, P¹CH₂), 2.36 (s, 3H, NMeeq), 2.43 (d, 3H, $^3J_{HH} = 7.2$ Hz, P²CCMe), 2.53-2.70 (m, 1H, P¹CHMe), 2.87 (s, 3H, NMeax), 4.49 (qn, 1H, $^3J_{HH} = ^4J_{PH} = 6.2$ Hz, CHMe), 6.46 (dd, 1H, $^3J_{PH} = ^3J_{HH} = 11.5$ Hz, P²CH), 6.98 (ddq, 1H, $^3J_{PH} = 38.1$ Hz, $^3J_{HH} = 11.5$ Hz, $^3J_{HH} = 7.2$ Hz, P²CCH), 7.30-7.92 (m, 21H, aromatics).

Synthesis of Regio-isomers 99b,d. The crude product 99b (0.40 g) was

redissolved in acetonitrile (25 mL) and slow recrystallized from acetonitrile and diethyl ether to give the 1:1 mixture of 99b,d as colorless crystals: 0.36 g (90% yield). mp 227 °C (dec); $[\alpha]_D -20$ (c 0.3, CHCl₃). Anal.Calcd for C₃₈H₄₂ClNO₄P₂Pd: C, 58.5; H, 5.4; N, 1.8. Found: C, 58.4; H, 5.5; N, 1.8. 4d: ³¹P NMR (CDCl₃) δ 15.9, 76.4 ($J_{PP} = 22.1$ Hz); ¹H-NMR (CDCl₃) δ 1.21 (dd, 3H, $^3J_{PH} = 12.1$ Hz, $^3J_{HH} = 6.9$ Hz, P¹CHMe), 1.71 (d, 3H, $^3J_{HH} = 6.2$ Hz, CHMe), 1.94 (d, 3H, $^3J_{HH} = 6.2$ Hz, P²CCMe), 1.94-2.20 (m, 2H, P¹CH₂), 2.36 (s, 3H, NMe_{eq}), 2.53-2.70 (m, 1H, P¹CHMe), 2.87 (s, 3H, NMe_{ax}), 4.55 (qn, 1H, $^3J_{HH} = ^4J_{PH} = 6.2$ Hz, CHMe), 6.35 (dd, 1H, $^3J_{PH} = ^3J_{HH} = 11.5$ Hz, P²CH), 6.76-7.09 (m, 1H, P²CCH), 7.30-8.34 (m, 21H, aromatics).

Synthesis of Complex 100a. Concentrate hydrochloric acid (10 mL) was added to a solution of 99a (0.29 g) in dichloromethane (25 mL). The reaction mixture was stirred vigorously at room temperature for 12 h, washed with water (3 × 20 mL) and dried (magnesium sulfate). Crystallization of the crude product from acetonitrile and diethyl ether gave the dichloro complex as yellowish crystals: 0.18 g (88% yield); mp: 250 °C (dec); $[\alpha]_D -88$ (c 0.6, CH₂Cl₂). Anal.Calcd for C₂₄H₂₆Cl₂P₂Pd: C, 52.1; H, 4.7. Found: C, 52.0; H, 5.0. ³¹P NMR (CDCl₃) δ 42.6, 75.2 ($J_{PP} = 6.3$ Hz). ¹H NMR (CDCl₃) δ 0.85 (dd, 3H, $^3J_{PH} = 14.6$ Hz, $^3J_{HH} = 7.1$ Hz, PCHMe), 1.98 (ddd, 3H, $^3J_{HH} = 7.1$ Hz, $^4J_{HH} = 1.5$ Hz, $^4J_{PH} = 3.0$ Hz, PCCMe), 2.11-2.41 (m, 2H, PCH₂), 2.95-3.14 (m, 1H, PCHMe), 5.91 (ddd, 1H, $^3J_{PH} = 15.5$ Hz, $^3J_{HH} = 12.1$ Hz, $^4J_{HH} = 1.5$ Hz, PCH), 6.74 (ddq, 1H, $^3J_{PH} = 41.2$ Hz, $^3J_{HH} = 12.1$ Hz, $^3J_{HH} = 7.1$ Hz, PCCH), 7.40-8.13 (m, 15H, aromatics).

Synthesis of Complex 100b. Concentrate hydrochloric acid (10 mL) was added to a solution of **99b** (0.30 g) in dichloromethane (25 mL). The reaction mixture was stirred vigorously at room temperature for 12 h, washed with water (3 × 20 mL) and dried (magnesium sulfate). Crystallization of the crude product from dichloromethane and diethyl ether gave the dichloro complex as yellowish crystals: 0.19 g (89% yield); mp: 260 °C; $[\alpha]_D -60$ (*c* 0.5, CH₂Cl₂). Anal. Calcd for C₂₄H₂₆Cl₂P₂Pd: C, 52.1; H, 4.7. Found: C, 52.0; H, 5.0. ³¹P NMR (CDCl₃) δ 39.7, 71.2 (*J*_{PP} = 5.6 Hz). ¹H NMR (CDCl₃) δ 1.14 (dd, 3H, ³*J*_{PH} = 13.2 Hz, ³*J*_{HH} = 6.9 Hz, PCHMe), 2.04 (ddd, 3H, ³*J*_{HH} = 7.1 Hz, ⁴*J*_{HH} = 1.3 Hz, ⁴*J*_{PH} = 2.9 Hz, PCCMe), 2.05-2.15 (m, 1H, PCHH'), 2.28-2.57 (m, 1H, PCHH'), 2.59-2.76 (m, 1H, PCHMe), 6.13 (ddd, 1H, ³*J*_{PH} = 20.1 Hz, ³*J*_{HH} = 12.2 Hz, ⁴*J*_{HH} = 1.3 Hz, PCH), 6.75 (ddq, 1H, ³*J*_{PH} = 41.6 Hz, ³*J*_{HH} = 12.2 Hz, ³*J*_{HH} = 7.1 Hz, PCCH), 7.41-8.05 (m, 15H, aromatics).

Liberation of free phosphine 101a. A solution of **100a** (0.06 g) in dichloromethane (20 mL) was stirred vigorously with a saturated aqueous solution of potassium cyanide (1 g) for 30 min. The colorless organic layer was separated, washed with water (3 × 20 mL), and dried (magnesium sulfate). Upon the removal of solvent, a white solid was obtained: 0.05 g (95% yield); $[\alpha]_{546} +70$ (*c* 0.5, CHCl₃). ³¹P NMR (CDCl₃) δ -44.8, 2.0 (*J*_{PP} = 20.8 Hz). ¹H NMR (CDCl₃) δ 1.21 (dd, 3H, ³*J*_{PH} = 15.4 Hz, ³*J*_{HH} = 6.8 Hz, PCHMe), 1.48-1.57 (m, 1H, PCHH'), 1.84 (d, 3H, ³*J*_{HH} = 6.8 Hz, PCCMe), 1.96-2.19 (m, 1H, PCHH'), 2.19-2.32 (m, 1H,

PCHMe), 5.94 (d, 1H, $^3J_{\text{PH}} = 11.5$ Hz, PCH), 6.29 (ddq, 1H, $^3J_{\text{PH}} = 21.7$ Hz, $^3J_{\text{HH}} = 11.5$ Hz, $^3J_{\text{HH}} = 6.8$ Hz, PCCH), 7.18-7.42 (m, 15H, aromatics).

Liberation of free phosphine 101b. A solution of **100b** (0.06 g) in dichloromethane (20 mL) was stirred vigorously with a saturated aqueous solution of potassium cyanide (1 g) for 30 min. The colorless organic layer was separated, washed with water (3×20 mL), and dried (magnesium sulfate). Upon the removal of solvent, a white solid was obtained: 0.05 g (95% yield); $[\alpha]_{\text{D}} +246$ (c 0.5, CHCl_3). ^{31}P NMR (CDCl_3) δ -46.5, 2.0 ($J_{\text{PP}} = 20.5$ Hz). ^1H NMR (CDCl_3) δ 1.22 (dd, 3H, $^3J_{\text{PH}} = 15.2$ Hz, $^3J_{\text{HH}} = 6.7$ Hz, PCHMe), 1.55-1.70 (m, 1H, PCHH'), 1.98 (d, 3H, $^3J_{\text{HH}} = 6.7$ Hz, PCCMe), 1.92-2.03 (m, 1H, PCHH'), 2.34-2.51 (m, 1H, PCHMe), 5.80 (dd, 1H, $^3J_{\text{PH}} = 22.5$ Hz, $^3J_{\text{HH}} = 11.3$ Hz, PCH), 6.51 (ddq, 1H, $^3J_{\text{PH}} = 21.7$ Hz, $^3J_{\text{HH}} = 11.3$ Hz, $^3J_{\text{HH}} = 6.7$ Hz, PCCH), 7.20-7.58 (m, 15H, aromatics).

Synthesis of Complexes 104a and 104c. Complex (*R*)-**102** (1.20 g) in dichloromethane (30mL) and aqueous silver perchlorate (0.80 g) were stirred vigorously at room temperature for 2 h. The mixture was filtered through Celite (to remove silver chloride), washed with water (3 X 30 mL), and dried (magnesium sulfate). The mixture was then degassed and treated with diphenylphosphine (0.35 g) at -78 °C for 12 h. By fractional crystallization, **104a** was isolated as colorless crystals from dichloromethane and diethyl ether: 0.48 g (30% yield). $[\alpha]_{\text{D}} -31$ (c 0.5, CH_2Cl_2), mp 204-205 °C (dec). Anal. Calcd for $\text{C}_{38}\text{H}_{42}\text{ClNO}_4\text{P}_2\text{Pd}$: C, 58.5; H, 5.4; N, 1.8. Found: C, 58.4; H, 5.5; N, 1.8. ^{31}P NMR (CDCl_3) δ 47.1, 48.0 ($J_{\text{PP}} =$

33.3 Hz); ^1H NMR (CDCl_3) δ 1.18 (dd, 3H, $^3J_{\text{PH}} = 11.6$ Hz, $^3J_{\text{HH}} = 6.8$ Hz, P^1CHMe), 1.95 (d, 3H, CHMe , $^3J_{\text{HH}} = 6.1$ Hz), 2.27 (ddd, 3H, $^3J_{\text{HH}} = 6.4$ Hz, $^4J_{\text{HH}} = ^4J_{\text{PH}} = 1.6$ Hz, P^2CCMe), 2.36 (dd, 3H, $^4J_{\text{PH}} = 3.9$ Hz, $^4J_{\text{P'H}} = 3.3$ Hz, NMeeq), 2.59 (d, 3H, $^4J_{\text{PH}} = 1.2$ Hz, NMeax), 2.86-2.91 (m, 2H, P^2CH_2), 3.70-3.88 (m, 1H, P^1CHMe), 4.48 (qn, 1H, $^3J_{\text{HH}} = ^4J_{\text{PH}} = 6.1$ Hz, CHMe), 6.62-6.69 (m, 1H, P^2CH), 7.14-7.20 (m, 1H, P^2CCH), 7.36-8.02 (m, 21H, aromatics). After isolation of the major product, the minor product **104c** subsequently crystallized from the concentrated mother liquid as colorless crystals: 0.21 g (13% yield). $[\alpha]_{\text{D}}^{-30}$ (c 0.5, CH_3Cl), mp 201-203 °C (dec). Anal. Calcd for $\text{C}_{38}\text{H}_{42}\text{ClINO}_4\text{P}_2\text{Pd}$: C, 58.5; H, 5.4; N, 1.8. Found: C, 58.4; H, 5.5; N, 1.8. ^{31}P NMR δ 46.5, 48.8 ($J_{\text{PP}} = 30.7$ Hz); ^1H NMR (CDCl_3) δ 1.18 (dd, 3H, $^3J_{\text{PH}} = 11.6$ Hz, $^3J_{\text{HH}} = 6.8$ Hz, P^1CHMe), 1.66 (d, 3H, CHMe , $^3J_{\text{HH}} = 6.2$ Hz), 1.98 (ddd, 3H, $^3J_{\text{HH}} = 6.4$ Hz, $^4J_{\text{HH}} = ^4J_{\text{PH}} = 1.6$ Hz, P^2CCMe), 2.28 (dd, 3H, $^4J_{\text{PH}} = 3.9$ Hz, $^4J_{\text{P'H}} = 3.3$ Hz, NMeeq), 2.88 (d, 3H, $^4J_{\text{PH}} = 1.2$ Hz, NMeax), 2.55-2.77 (m, 2H, P^2CH_2), 3.72-3.76 (m, 1H, P^1CHMe), 4.40 (qn, 1H, $^3J_{\text{HH}} = ^4J_{\text{PH}} = 6.1$ Hz, CHMe), 6.25-6.35 (m, 1H, P^2CH), 7.20-7.24 (m, 1H, P^2CCH), 7.36-8.02 (m, 21H, aromatics).

Synthesis of Complex 105a. Concentrate hydrochloric acid (10 mL) was added to a solution of **104a** (0.29 g) in dichloromethane (25 mL). The reaction mixture was stirred vigorously at room temperature for 12 h, washed with water (3×20 mL) and dried (magnesium sulfate). Crystallization of the crude product from acetonitrile and diethyl ether gave the dichloro complex as yellowish crystals: 0.17 g (85% yield); Anal. Calcd for $\text{C}_{24}\text{H}_{26}\text{Cl}_2\text{P}_2\text{Pd}$: C, 52.1; H, 4.7. Found: C, 52.0; H,

5.0. ^{31}P NMR (CDCl_3) δ 49.0, 72.6 ($J_{\text{PP}} = 5.1\text{ Hz}$); ^1H NMR (CDCl_3) δ 1.04 (dd, 3H, $^3J_{\text{PH}} = 13.8\text{ Hz}$, $^3J_{\text{HH}} = 6.9\text{ Hz}$, P^1CHMe), 1.99 (ddd, 3H, $^3J_{\text{HH}} = 6.5\text{ Hz}$, $^4J_{\text{HH}} = ^4J_{\text{PH}} = 1.6\text{ Hz}$, P^2CCMe), 2.23-2.33 (m, 1H, P^2CH), 2.38-2.48 (m, 1H, $\text{P}^2\text{CH}'$), 2.91-3.01 (m, 1H, P^1CHMe), 6.07 (ddq, 1H, $^3J_{\text{PH}} = 17.4\text{ Hz}$, $^3J_{\text{HH}} = 16.5\text{ Hz}$, $^4J_{\text{HH}} = 1.6\text{ Hz}$, P^2CH), 7.01 (ddq, 1H, $^3J_{\text{PH}} = 20.5\text{ Hz}$, $^3J_{\text{HH}} = 16.5\text{ Hz}$, $^3J_{\text{HH}} = 6.5\text{ Hz}$, P^2CCH), 7.44-7.96 (m, 15H, aromatics).

Synthesis of Complex 105b. The hydrophosphination reaction mother liquid apart from **104a** and **104c** (0.29 g) was treated with concentrate hydrochloric acid (10 mL) and stirred vigorously overnight, washed with water ($3 \times 20\text{ mL}$) and dried (magnesium sulfate). Crystallization of the crude product from acetonitrile and diethyl ether gave the dichloro complex as yellowish crystals: 0.12 g (58% yield); Anal. Calcd for $\text{C}_{24}\text{H}_{26}\text{Cl}_2\text{P}_2\text{Pd}$: C, 52.1; H, 4.7. Found: C, 52.0; H, 5.0. ^{31}P NMR (CDCl_3) δ 48.4, 71.2 ($J_{\text{PP}} = 5.2\text{ Hz}$); ^1H NMR (CDCl_3) δ 1.04 (dd, 3H, $^3J_{\text{PH}} = 13.8\text{ Hz}$, $^3J_{\text{HH}} = 6.9\text{ Hz}$, P^1CHMe), 1.99 (ddd, 3H, $^3J_{\text{HH}} = 6.5\text{ Hz}$, $^4J_{\text{HH}} = ^4J_{\text{PH}} = 1.6\text{ Hz}$, P^2CCMe), 2.23-2.33 (m, 1H, P^2CH), 2.38-2.48 (m, 1H, $\text{P}^2\text{CH}'$), 2.74-2.85 (m, 1H, P^1CHMe), 6.45 (ddq, 1H, $^3J_{\text{PH}} = 21.6\text{ Hz}$, $^3J_{\text{HH}} = 16.5\text{ Hz}$, $^4J_{\text{HH}} = 1.6\text{ Hz}$, P^2CH), 6.77 (ddq, 1H, $^3J_{\text{PH}} = 19.6\text{ Hz}$, $^3J_{\text{HH}} = 16.5\text{ Hz}$, $^3J_{\text{HH}} = 6.5\text{ Hz}$, P^2CCH), 7.44-7.96 (m, 15H, aromatics).

Synthesis of Complex 105c. Concentrate hydrochloric acid (10 mL) was added to a solution of **104c** (0.29 g) in dichloromethane (25 mL). The reaction mixture was stirred vigorously at room temperature for 12 h, washed with water ($3 \times 20\text{ mL}$)

and dried (magnesium sulfate). Crystallization of the crude product from acetonitrile and diethyl ether gave the dichloro complex as yellowish crystals: 0.17 g (85% yield); Anal. Calcd for $C_{24}H_{26}Cl_2P_2Pd$: C, 52.1; H, 4.7. Found: C, 52.0; H, 5.0. ^{31}P NMR ($CDCl_3$) δ 49.0, 72.6 ($J_{PP} = 5.1$ Hz); 1H NMR ($CDCl_3$) δ 1.04 (dd, 3H, $^3J_{PH} = 13.8$ Hz, $^3J_{HH} = 6.9$ Hz, P^1CHMe), 1.99 (ddd, 3H, $^3J_{HH} = 6.5$ Hz, $^4J_{HH} = ^4J_{PH} = 1.6$ Hz, P^2CCMe), 2.23-2.33 (m, 1H, P^2CH), 2.38-2.48 (m, 1H, P^2CH'), 2.91-3.01 (m, 1H, P^1CHMe), 6.07 (ddq, 1H, $^3J_{PH} = 17.4$ Hz, $^3J_{HH} = 16.5$ Hz, $^4J_{HH} = 1.6$ Hz, P^2CH), 7.01 (ddq, 1H, $^3J_{PH} = 20.5$ Hz, $^3J_{HH} = 16.5$ Hz, $^3J_{HH} = 6.5$ Hz, P^2CCH), 7.44-7.96 (m, 15H, aromatics).

Crystal Structure Determinations of Complexes 99a, 99b,d, 104a, 104c, 105a, 105b, and 105c. Diffraction data were collected at the Nanyang Technological University using a Bruker X8 Apex diffractometer with Mo K α radiation (graphite monochromator). All non-H atoms were refined anisotropically, while Hydrogen atoms were introduced at a fixed distance from the carbon atoms and were assigned fixed thermal parameters. The absolute configurations of the chiral complexes were determined unambiguously using the Flack parameter.¹¹⁰

Chapter 5

Base Controlled (1,1)- and (1,2)-Hydrophosphination of Functionalized Alkynes

5.1 Introduction

The synthesis of functionalized chiral phosphines is considered as important task since these ligands play vital roles in transition metal catalyzed reactions.¹¹⁵ The addition of secondary phosphines to carbon-carbon multiple bonds is generally considered a straightforward and efficient organic synthetic process.¹¹⁶ However, this approach continues to pose considerable challenges in the preparation of oxygen-sensitive and highly reactive phosphines. Transition metal complex-assisted hydrophosphination reactions have been reported.¹¹⁷ In general, metal complexes offer better stabilization and selectivity in hydrophosphination reactions than other reaction promoters such as strong bases,⁶⁹ acids,⁶⁸ and free radicals.^{72, 118} Our group has previously reported a series of chiral complex-promoted asymmetric 1,2-addition reactions with alkynes in the absence of external base promoters.⁸²⁻⁸⁴ This chapter describes the preparation of functionalized diphosphines from substituted alkynes via a simple chiral palladium template-promoted hydrophosphination reaction. By regulating the amount of triethylamine, as a mild external base, the (1,1)- and (1,2)-addition pathways could be controlled chemoselectively. It is important to note that the functionalized 1,1-diphosphine products could not be produced by the traditional addition reaction using 1,1-bis(diphenylphosphino)-ethylene as the starting material.¹¹⁹

5.2 Results and Discussion

5.2.1 Base Controlled (1,1)- and (1,2)-Hydrophosphination of 3-Butyn-2-one

In the absence of triethylamine, diphenylphosphine shows no reactivity towards the functionalized alkyne 3-Butyn-2-one **106** under ambient conditions, even in the presence of the standard chiral reaction promoter (*R*)-**79**.⁷ In the presence of 2 mol% of triethylamine and the chiral palladium complex (*R*)-**79**, the reaction between diphenylphosphine and 3-butyn-2-one **106** proceeded smoothly at -78 °C generating a 1:2 mixture of the stereoisomeric 1,1-addition products **107a** and **107b** regioselectively (Scheme 5.1).

Scheme 5.1

The keto groups in these two isomeric product complexes are located on the opposite side of the square-plane. Prior to purification, the ^{31}P NMR spectrum of the crude reaction product in CDCl_3 exhibited two pairs of doublets at δ -18.8, 9.6

($J_{\text{PP}} = 52$ Hz, minor product) and -18.5, 8.2 ($J_{\text{PP}} = 54$ Hz, major product), respectively. The 202 MHz ^{31}P NMR spectrum did not detect the presence of any sterically favorable (1,2)-addition products in the crude mixture. The isomeric mixture was then treated with concentrated hydrochloric acid to remove the chiral naphthylamine ligand to afford a single dichloro complex **108** in 85% yield. The ^{31}P NMR spectrum of **108** in CD_2Cl_2 exhibited a sharp singlet at δ -37.5. The X-ray structure of **108** is shown in Figure 5.1. Selected bond lengths and angles are given in Table 5.1. Interestingly, both the $\text{P}(1)\text{-C}(13)\text{-P}(2)$ [$92.8(1)^\circ$] and the $\text{P}(1)\text{-Pd}(1)\text{-P}(2)$ [$74.5(1)^\circ$] angles within the 4-membered ring are both rather small. Treatment of a CH_2Cl_2 solution of **108** with aqueous potassium cyanide liberated the keto-substituted diphosphine **109** as a white solid in 95% yield. The ^{31}P NMR spectrum of the liberated ligand in CDCl_3 exhibited a sharp singlet at δ -5.3.

Figure 5.1. Molecular structure and absolute stereochemistry of complex **108**.

Table 5.1. Selected Bond Lengths (Å) and Bond Angles (deg) of **108**

Pd(1)-P(2)	2.2289(5)
Pd(1)-P(1)	2.2322(6)
Pd(1)-Cl(1)	2.3494(7)
Pd(1)-Cl(2)	2.3544(8)
P(1)-C(13)	1.8654(19)
P(2)-C(13)	1.8639(19)
C(13)-C(14)	1.528(3)
C(14)-C(15)	1.520(3)
P(2)-Pd(1)-P(1)	74.534(19)
P(2)-C(13)-P(1)	92.83(9)
P(2)-Pd(1)-Cl(1)	171.79(3)
P(1)-Pd(1)-Cl(1)	97.28(3)
P(2)-Pd(1)-Cl(2)	94.31(3)
P(1)-Pd(1)-Cl(2)	168.52(3)
Cl(1)-Pd(1)-Cl(2)	93.84(3)

Interestingly, when the above hydrophosphination of 3-butyne-2-one **106** was performed under similar reaction conditions but in the presence of excess triethylamine (20 equiv.), the reaction proceeded exclusively *via* the (1,2)-addition pathway (Scheme 5.2).

Scheme 5.2

Figure 5.2. Molecular structure and absolute stereochemistry of complex **110a**.

Table 5.2. Selected Bond Lengths (Å) and Bond Angles (deg) of **110a**

Pd(1)-C(1)	2.042(11)
Pd(1)-N(1)	2.141(6)
Pd(1)-P(1)	2.246(2)
Pd(1)-P(2)	2.345(3)
C(16)-P(2)	1.860(9)
C(15)-C(16)	1.534(13)
C(15)-P(1)	1.822(10)
C(16)-C(17)	1.496(15)
C(1)-Pd(1)-N(1)	80.8(4)
C(1)-Pd(1)-P(1)	96.0(3)
N(1)-Pd(1)-P(1)	176.0(3)

C(1)-Pd(1)-P(2)	177.8(3)
N(1)-Pd(1)-P(2)	98.3(2)
P(1)-Pd(1)-P(2)	84.82(9)

In CDCl₃, the 202 MHz ³¹P NMR spectrum of the crude mixture indicated the four diastereomeric (1,2)-addition products only: four pairs of doublets were recorded with the intensity ratio of *ca* 7:1:1:1 at δ 45.1, 48.9 ($J_{\text{PP}} = 32$ Hz, major signals); 45.4, 48.3 ($J_{\text{PP}} = 32$ Hz); 29.2, 64.2 ($J_{\text{PP}} = 32$ Hz) and 41.0, 70.5 ($J_{\text{PP}} = 22$ Hz), respectively. Thus the spectroscopic study revealed that all the four possible diastereomeric 1,2-addition products **110a-d** were generated in the hydrophosphination reaction. The major isomer **110a** was subsequently crystallized from acetone-diethyl ether as pale yellow prisms in 40% yield. The molecular structures and the absolute stereochemistry of **110a** were determined by X-ray crystallography (Figure 5.2). Selected bond lengths and angles are given in Table 5.2. The absolute chirality at C(16) is *S*. The P(2)-Pd(1)-P(1) bond angle [84.8(1)°] in **110a** is significantly larger than its counterpart in complex **108**. Unfortunately, treatment of **110a** with concentrated hydrochloric acid generated the *racemic* dichloro complex **111** in 90% yield (Scheme 5.3). The 202 MHz ³¹P NMR spectrum of **111** in CDCl₃ exhibited a pair of doublets at δ 47.4, 70.6 ($J_{\text{PP}} = 9$ Hz). The molecular structures and the absolute stereochemistry of **111** were determined by X-ray crystallography (Figure 5.3). Selected bond lengths and angles are given in Table 5.3.

Scheme 5.3

Figure 5.3. Molecular structure and absolute stereochemistry of complex **111**.

Table 5.3. Selected Bond Lengths (Å) and Bond Angles (deg) of **111**

Pd(1)-Cl(1)	2.3602(8)
Pd(1)-Cl(2)	2.3534(8)
Pd(1)-P(1)	2.2306(7)
Pd(1)-P(2)	2.2343(8)

C(1)-P(1)	1.827(3)
C(2)-P(2)	1.877(3)
C(2)-C(3)	1.533(4)
Cl(1)-Pd(1)-Cl(2)	94.16(3)
Cl(1)-Pd(1)-P(1)	174.99(3)
Cl(2)-Pd(1)-P(1)	90.83(3)
Cl(1)-Pd(1)-P(2)	88.98(3)
Cl(2)-Pd(1)-P(2)	174.05(3)
P(1)-Pd(1)-P(2)	86.01(3)

The racemization of the chiral keto-substituted diphosphine ligand is attributed to the keto-enol tautomerism of the carbonyl functionality during the acid treatment (Scheme 5.3.1). This stereo-dynamic process readily disturbed the chirality of the stereogenic carbon centre in the chiral diphosphine ligand.

Scheme 5.3.1

5.2.2 Base Controlled (1,1)- and (1,2)-Hydrophosphination of Ethyl propiolate

In order to avoid the intrinsic problem of racemization, the keto group in the original alkyne was replaced by its ester analogue. Thus, in the presence of excess triethylamine (2 equiv.), the hydrophosphination of ethyl propiolate **112** at -78 °C gave only three of the four possible (1,2)-addition diastereomeric products (Scheme 5.4).

Scheme 5.4

In CDCl₃, the 202 MHz ³¹P NMR spectrum of the crude product showed three pairs of doublets with the intensity ratio of *ca* 18:3:1 at δ 47.6, 48.9 ($J_{\text{PP}} = 32$ Hz); 28.5, 66.4 ($J_{\text{PP}} = 33$ Hz) and 35.4, 69.9 ($J_{\text{PP}} = 26$ Hz), respectively. The major product **113a** was isolated from dichloromethane-diethyl ether as pale yellow prisms in 55% yield. The molecular structures and the absolute stereochemistry of **113a** were determined by X-ray crystallography (Figure 5.4). Selected bond lengths and angles are given in Table 5.4.

Figure 5.4. Molecular structure and absolute stereochemistry of **113a**.

Table 5.4 Selected Bond Lengths (Å) and Bond Angles (deg) of **113a**

Pd(1)-C(1)	2.063(5)
Pd(1)-N(1)	2.162(5)
Pd(1)-P(2)	2.2440(14)
Pd(1)-P(1)	2.3814(13)
P(1)-C(27)	1.871(6)
P(2)-C(31)	1.833(5)
C(27)-C(28)	1.528(8)
C(27)-C(31)	1.532(8)
C(1)-Pd(1)-N(1)	79.4(2)
C(1)-Pd(1)-P(2)	97.44(16)
N(1)-Pd(1)-P(2)	176.62(13)
C(1)-Pd(1)-P(1)	179.16(16)
N(1)-Pd(1)-P(1)	99.80(13)
P(2)-Pd(1)-P(1)	83.33(5)

Treatment of complex **113a** with concentrated hydrochloric acid gave the enantiomerically pure dichloro complex **114** in 90% yield, with $[\alpha]_{436} -78$ (c 0.5, CH_2Cl_2). In contrast to its keto-analogue, the absolute stereochemistry of the chiral diphosphine ligand in **114** remained unchanged during the acidic treatment, as the ester group was not involved in a similar tautomerism process. The molecular structures and the absolute stereochemistry of **113a** were determined by X-ray crystallography (Figure 5.5). Selected bond lengths and angles are given in Table 5.5. As shown in Scheme 5.5, treatment of a CH_2Cl_2 solution of **114** with aqueous potassium cyanide liberated the optically pure diphosphine **115** as a white solid in 95% yield, with $[\alpha]_{436} -33$ (c 1.0, CH_3Cl , 24 °C). The ^{31}P NMR spectrum of the free diphosphine in CDCl_3 exhibited a pair of doublets at δ -16.6, 2.4 ($J_{\text{PP}} = 24$ Hz).

Scheme 5.5

Figure 5.5. Molecular structure and absolute stereochemistry of complex **114**.

Table 5.5 Selected Bond Lengths (Å) and Bond Angles (deg) of **114**

Pd(1)-Cl(1)	2.3562(6)
Pd(1)-Cl(2)	2.3620(6)
Pd(1)-P(2)	2.2313(5)
Pd(1)-P(1)	2.2382(6)
P(1)-C(13)	1.8823(16)
P(2)-C(17)	1.8325(18)
C(13)-C(17)	1.524(2)
Cl(1)-Pd(1)-Cl(2)	94.70(2)
Cl(1)-Pd(1)-P(2)	173.93(3)
Cl(2)-Pd(1)-P(2)	90.29(2)
Cl(1)-Pd(1)-P(1)	89.02(2)
Cl(2)-Pd(1)-P(1)	171.143(19)
P(2)-Pd(1)-P(1)	86.53(2)

The optical purity of the liberated chiral diphosphine was confirmed by the quantitative recoordination of **115** to (*R*)-**79**: the 202 MHz ^{31}P NMR spectrum of the crude product showed only two pairs of doublets with similar intensity at δ 47.6, 48.9 ($J_{\text{PP}} = 32$ Hz) and 28.5, 66.4 ($J_{\text{PP}} = 33$ Hz). The spectroscopic signals confirmed the formation of **113a** and its regio-isomer **113c**. In a further test of optical purity, the diastereomers **116** and **117** were prepared from **115** and the equally accessible (*S*)-**79** (Scheme 5.6). The ^{31}P NMR spectrum of the crude product showed two clearly different pairs of doublets with similar intensity at δ 35.4, 69.9 ($J_{\text{PP}} = 26$ Hz) and 47.5, 47.9 ($J_{\text{PP}} = 31$ Hz).

Scheme 5.6

Interestingly, the reaction rate and the (1,1)- and (1,2)-chemoselectivity of the hydrophosphination reaction is sensitive to the functionality present on the reacting alkyne. The ester-substituted alkyne **112** appeared to favour the (1,2)-addition pathway. Thus when the amount of triethylamine was reduced to 2 mol%, the hydrophosphination reaction between diphenylphosphine and **112** at -78 °C continued to give mostly the (1,2)-addition products. In contrast to the similar

reaction involving the keto-alkyne **106**, only a small quantity of (1,1)-addition ester products, together with some as yet unidentified materials were generated under these conditions. The optimum condition for the synthesis of the (1,1)-addition products required the presence of 20 mol% of triethylamine and the reaction was conducted at room temperature. Under these conditions, a 2:3 mixture of the two stereoisomeric (1,1)-addition products **118a** and **118b** could be obtained in 50% isolated yield (Scheme 5.7).

Treatment of the mixture with concentrated hydrochloric acid generated a single dichloro complex **119**, quantitatively. The molecular structures and the coordination chemistry of **113a** were determined by X-ray crystallography (Figure 5.6). Selected bond lengths and angles are given in Table 5.6. As shown in Figure 5.6, the X-ray structural analysis of **119** revealed that it has a similar molecular

orientation to its keto counterpart **108**. There are no major steric repulsions around the ester functional group in **119**. Thus, apart from the quantity of the external base used, the electronic properties of the functional group in the substituted-alkynes also plays a major role in reaction mechanism of the current hydrophosphination reaction for the chemoselective formation of the (1,1)- and (1,2)-addition products.

Figure 5.6. Molecular structure and absolute stereochemistry of complex **119**.

Table 5.6. Selected Bond Lengths (Å) and Bond Angles (deg) of **119**

Pd(1)-P(1)	2.2207(8)
Pd(1)-P(2)	2.2382(9)
Pd(1)-Cl(1)	2.3607(10)
Pd(1)-Cl(2)	2.3622(9)
P(1)-C(13)	1.866(3)
P(2)-C(13)	1.871(3)

C(13)-C(14)	1.536(5)
C(14)-C(15)	1.528(5)
P(1)-Pd(1)-P(2)	74.23(3)
P(1)-C(13)-P(2)	92.10(15)
P(1)-Pd(1)-Cl(1)	93.58(4)
P(2)-Pd(1)-Cl(1)	167.73(4)
P(1)-Pd(1)-Cl(2)	172.76(4)
P(2)-Pd(1)-Cl(2)	98.54(4)
Cl(1)-Pd(1)-Cl(2)	93.65(4)

5.2.3 Hydrophosphination Reaction Between Phenylmethylphosphine and Diethyl acetylenedicarboxylate

In order to compare the addition selectivity between diphenylphosphine and phenylmethylphosphine, hydrophosphination reaction between phenylmethylphosphine and diethyl acetylenedicarboxylate was explored.

As illustrated in Scheme 5.8, phenylmethylphosphine was coordinated to complex (*R*)-**79** at room temperature. The ^{31}P NMR spectrum of crude product in CD_2Cl_2 exhibited four pairs of doublets of doublets with the ratio 2.3: 2.3: 1.8: 1: δ -29.2, -9.6 ($J_{\text{PP}} = 45.0$ Hz); -30.9, -9.5 ($J_{\text{PP}} = 42.3$ Hz); -32.1, -4.7 ($J_{\text{PP}} = 43.3$ Hz) and -30.2, -6.1 ($J_{\text{PP}} = 42.2$ Hz).

Scheme 5.8

As shown in Scheme 5.9, in the presence of 5 mol% of triethylamine and the chiral palladium complex (R)-79, the reaction between phenylmethylphosphine and DEADC proceeded smoothly at -78 °C. In CDCl₃, the 202 MHz ³¹P NMR spectrum of the crude mixture indicated three major diastereomeric (1,2)-addition products: three pairs of doublets were recorded with the intensity ratio of *ca* 1.7:1:1 at δ 39.4, 46.0 ($J_{\text{PP}} = 37.9$ Hz); 20.3, 47.7 ($J_{\text{PP}} = 38.3$ Hz) and 20.8, 37.8 ($J_{\text{PP}} = 36.9$ Hz), respectively. However, the cationic diastereomers could not be separated efficiently by chromatography or fractional crystallization.

Scheme 5.9

5.2.4 Base Controlled (1,1) -Hydrophosphination Reaction between Phenylmethylphosphine and 3-Butyn-2-one

As shown in Scheme 5.10, in the presence of 5 mol% of triethylamine and the chiral palladium complex **(R)-79**, the reaction between phenylmethylphosphine and 3-butyne-2-one **106** proceeded smoothly at $-78\text{ }^{\circ}\text{C}$. In CDCl_3 , the 202 MHz ^{31}P NMR spectrum of the crude mixture indicated three major diastereomeric (1,1)-

addition products: six pairs of doublets were recorded with the intensity ratio of *ca* 2.4 : 2.4 : 1.8 : 1.6 : 1.1 : 1 at δ -34.1, 3.3 ($J_{\text{PP}} = 63.5$ Hz); -32.4, 0.0 ($J_{\text{PP}} = 66.4$ Hz); -27.0, -8.0 ($J_{\text{PP}} = 64.5$ Hz); -30.9, -7.1 ($J_{\text{PP}} = 66.2$ Hz); -32.3, -5.8 ($J_{\text{PP}} = 63.4$ Hz) and -29.1, -4.6 ($J_{\text{PP}} = 66.2$ Hz). Unfortunately, the cationic diastereomers could not be separated efficiently by chromatography or fractional crystallization.

Scheme 5.10

5.3 Conclusion

The (1,1)- and (1,2)-addition of diphenylphosphine to 3-butyne-2-one and ethyl propiolate controlled chemoselectively by regulating the amount of triethylamine as the external base and in the presence of the chiral organopalladium(II) template derived from (*R*)-*N,N*-dimethyl-1-(1-naphthyl)ethylamine are demonstrated in this chapter. The hydrophosphination of Diethyl acetylenedicarboxylate (DMADC) and 3-butyne-2-one with phenylmethylphosphine could not obtain high selectivity under similar reaction conditions.

5.4 Experimental Section

Reactions involving air-sensitive compounds were performed under a positive pressure of purified 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 0.1 dm cell at 25 °C with a Perkin-Elmer model 341 polarimeter. Elemental analyses were performed by the staff in the Elemental Analysis Laboratory of the Division of Chemical and Biological Chemistry of Nanyang Technological University. Melting points were measured using the SRS OptiMelt Automated Melting Point System, SRS MPA100.

All solvents used for the synthesis of ligands and reactions were deoxygenated using a positive pressure of argon. Analytical-grade chemicals were purchased from Sigma-Aldrich and Strem Chemicals.

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

Synthesis of Complex 108. A mixture of 3-butyne-2-one (0.136 g), diphenylphosphine (0.075 g), triethylamine (0.004 g) and (*R*)-**79** (0.972 g) in dichloromethane (100 mL) was stirred at -78 °C for 12 h. Concentrated HCl (15 mL) was added to the solution and stirred vigorously at room temperature for 12 h, washed with water (3 X 20 mL), and dried (MgSO₄). Crystallization of the crude product from dichloromethane and diethyl ether gave the dichloro complex as yellow crystals, 1.050 g (85% yield). mp 212-214 °C (dec.). Anal. Calcd for C₂₈H₂₆Cl₂OP₂Pd: C, 54.4; H, 4.2%. Found: C, 54.1; H, 4.0%. ³¹P NMR (CD₂Cl₂) δ -37.5; ¹H NMR (CD₂Cl₂) δ 1.42 (s, 3H, COMe), 2.23 (dt, 2H, ³J_{HH} = 7.6 Hz, J_{PH} = 15.1 Hz, PCCH₂), 5.23 (tt, 1H, ³J_{HH} = 7.6 Hz, J_{PH} = 10.6 Hz, PCH), 7.44-8.17 (m, 20H, aromatics).

Liberation of Complex 109. A solution of **108** (0.074 g) in dichloromethane was stirred vigorously with a saturated aqueous solution of potassium cyanide (1.00 g) for 2 h. The organic layer was separated, washed with water (3 X 20 mL), and dried (MgSO₄). Upon removal of solvent, a white solid was obtained: 0.050 g (95% yield). ³¹P NMR (CDCl₃) δ -5.3; ¹H NMR (CD₂Cl₂) δ 1.36 (s, 3H, COMe), 2.53 (dt, 2H, ³J_{HH} = 5.4 Hz, J_{PH} = 9.1 Hz, PCCH₂), 4.19 (tt, 1H, ³J_{HH} = J_{PH} = 5.4 Hz, PCH), 7.25-7.56 (m, 20H, aromatics).

Synthesis of Complex 110a. A mixture of 3-butyne-2-one (0.136 g), diphenylphosphine (0.075 g), triethylamine (4.050 g) and (*R*)-**79** (0.972 g) in dichloromethane (100 mL) was stirred at room temperature for 12 h. The solvent was removed and complex **110a** was obtained from dichloromethane and diethyl ether as colorless crystals, 0.705 g (40% yield). mp 203-204 °C (dec.); $[\alpha]_D -58$ (*c* 0.5, CH₂Cl₂). Anal. Calcd for C₄₂H₄₂ClNO₅P₂Pd: C, 59.7; H, 5.0; N, 1.7%. Found: C, 59.2; H, 5.4; N, 1.6%. ³¹P NMR (CDCl₃) δ 45.1, 48.9 ($J_{PP} = 33$ Hz); ¹H NMR (CDCl₃) δ 1.88 (s, 3H, COMe), 1.95 (d, 3H, ³ $J_{HH} = 6.1$ Hz, CHMe), 2.43 (d, 3H, $J_{PH} = 1.2$ Hz, NMe_{eq}), 2.51 (dd, 3H, $J_{PH} = J_{PH} = 3.7$ Hz, NMe_{ax}), 2.76-2.88 (m, 1H, P²CHH'), 2.95-3.06 (m, 1H, P²CHH'), 3.77-3.88 (m, 1H, P¹CHCOMe), 4.48 (qn, 1H, ³ $J_{HH} = ^4J_{PH} = 6.1$ Hz, CHMe), 6.87-8.19 (m, 26H, aromatics).

Synthesis of Complex 111. Concentrated HCl (10 mL) was added to a solution of **110a** (0.200 g) in dichloromethane (30 mL). The reaction mixture was stirred vigorously at room temperature for 12 h, washed with water (3 X 20 mL), and dried (MgSO₄). Crystallization of the crude product from dichloromethane and diethyl ether gave the dichloro complex as yellow crystals, 0.126 g (90% yield). mp 188-189 °C (dec.). Anal. Calcd for C₂₈H₂₆Cl₂OP₂Pd: C, 54.4; H, 4.2%. Found: C, 54.1; H, 4.0%. ³¹P NMR (CDCl₃) δ 47.4, 70.6 ($J_{PP} = 9$ Hz); ¹H NMR (CDCl₃) δ 1.80 (s, 3H, COMe), 2.57-2.68 (m, 1H, P²CHH'), 2.75-2.87 (m, 1H, P²CHH'), 3.66-3.78 (m, 1H, P¹CHCOMe), 7.46-8.15 (m, 20H, aromatics).

Synthesis of Complex 113a. A mixture of ethyl propiolate (0.196 g), diphenylphosphine (0.075 g), triethylamine (0.405 g) and (*R*)-**79** (0.972 g) in dichloromethane (100 mL) was stirred at -78 °C for 12 h. The solvent was removed and complex **113a** was obtained from dichloromethane and diethyl ether as colorless crystals, 1.008 g (55% yield). mp 182-184 °C (dec.); $[\alpha]_D -110$ (*c* 0.5, CH₂Cl₂). Anal. Calcd for C₄₃H₄₄ClNO₆P₂Pd: C, 59.0; H, 5.1; N, 1.6%. Found: C, 58.6; H, 5.2; N, 1.6%. ³¹P NMR (CDCl₃) δ 47.6, 48.9 (*J*_{PP} = 32 Hz); ¹H NMR (CDCl₃) δ 0.87 (t, 3H, ³*J*_{HH} = 7.1 Hz, COOCH₂CH₃), 1.96 (d, 3H, ³*J*_{HH} = 6.2 Hz, CHMe), 2.48 (d, 3H, *J*_{PH} = 1.2 Hz, NMe_{eq}), 2.61 (dd, 3H, *J*_{PH} = *J*_{PH} = 3.7 Hz, NMe_{ax}), 2.89-3.00 (m, 1H, P²CHH'), 3.06-3.16 (m, 1H, P²CHH'), 3.17-3.29 (m, 1H, P¹CHCOOEt), 3.78-3.94 (m, 2H, COOCH₂CH₃), 4.55 (qn, 1H, ³*J*_{HH} = ⁴*J*_{PH} = 6.2 Hz, CHMe), 6.87-8.26 (m, 26H, aromatics).

Synthesis of Complex 114. Concentrated HCl (10 mL) was added to a solution of **110a** (0.200 g) in dichloromethane (30 mL). The reaction mixture was stirred vigorously at room temperature for 12 h, washed with water (3 X 20 mL), and dried (MgSO₄). Crystallization of the crude product from dichloromethane and diethyl ether gave the dichloro complex as yellow crystals, 0.127 g (90% yield). mp 257-258 °C (dec.); $[\alpha]_{436} -78$ (*c* 0.5, CH₂Cl₂). Anal. Calcd for C₂₉H₂₈Cl₂O₂P₂Pd: C, 53.8; H, 4.4%. Found: C, 53.4; H, 4.4%. ³¹P NMR (CDCl₃) δ 49.0, 73.6 (*J*_{PP} = 9 Hz); ¹H NMR (CDCl₃) δ 0.90 (t, 3H, ³*J*_{HH} = 7.1 Hz, COOCH₂CH₃), 2.72-3.01 (m, 2H, PCH₂CHCOOEt), 3.47-3.61 (m, 1H, PCHCOOEt), 3.82-3.85 (m, 2H, COOCH₂CH₃), 7.43-8.13 (m, 20H, aromatics).

Liberation of Free Ligand 115. A solution of **114** (0.073 g) in dichloromethane was stirred vigorously with a saturated aqueous solution of potassium cyanide (1.00 g) for 2 h. The organic layer was separated, washed with water (3 X 20 mL), and dried (MgSO₄). Upon removal of solvent, a white solid was obtained: 0.050 g (95% yield). $[\alpha]_{436} -33$ (*c* 1.0, CH₃Cl). ³¹P NMR (CDCl₃) δ -16.6, 2.4 ($J_{PP} = 24$ Hz); ¹H NMR(CDCl₃) δ 0.93 (t, 3H, $^3J_{HH} = 7.1$ Hz, COOCH₂CH₃), 2.16-2.26 (m, 1H, PCH'HCHCOOEt), 2.60-2.73 (m, 1H, PCH'HCHCOOEt), 3.19-3.28 (m, 1H, PCHCOOEt), 3.68-3.89 (m, 2H, COOCH₂CH₃), 7.26-7.38 (m, 20H, aromatics).

Synthesis of Complex 119. A mixture of ethyl propiolate (0.196 g), diphenylphosphine (0.075 g), triethylamine (0.040 g) and (*R*)-**79** (0.972 g) in dichloromethane (100 mL) was stirred at room temperature for 12 h. Concentrated HCl (15 mL) was added to the solution and stirred vigorously at room temperature for 12 h, washed with water (3 X 20 mL), and dried (MgSO₄). Crystallization of the crude product from dichloromethane and diethyl ether gave the dichloro complex as yellow crystals, 1.100 g (85% yield). mp 197-199 °C (dec.). Anal.Calcd for C₂₉H₂₈Cl₂O₂P₂Pd: C, 53.8; H, 4.4%. Found: C, 53.5; H, 4.6%. ³¹P NMR (CDCl₃) δ -37.3; ¹H NMR (CDCl₃) δ 0.98 (t, 3H, $^3J_{HH} = 7.1$ Hz, COOCH₂CH₃), 2.20 (dt, 2H, $^3J_{HH} = 8.0$ Hz, $J_{PH} = 15.1$ Hz, PCCH₂), 3.81 (q, 2H, $^3J_{HH} = 7.1$ Hz, COOCH₂CH₃), 5.19 (tt, 1H, $^3J_{HH} = 8.0$ Hz, $J_{PH} = 10.6$ Hz, PCH), 7.48-8.24 (m, 20H, aromatics).

Liberation of Free Ligand 120. A solution of **119** (0.073 g) in dichloromethane was stirred vigorously with a saturated aqueous solution of potassium cyanide (1.00 g) for 2 h. The organic layer was separated, washed with water (3 X 20 mL), and dried (MgSO_4). Upon removal of solvent, a white solid was obtained: 0.050 g (95% yield). ^{31}P NMR (CDCl_3) δ -5.9; ^1H NMR (CDCl_3) δ 0.96 (t, 3H, $^3J_{\text{HH}} = 7.2$ Hz, $\text{COOCH}_2\text{CH}_3$), 2.41 (dt, 2H, $^3J_{\text{HH}} = 5.9$ Hz, $J_{\text{PH}} = 9.2$ Hz, PCCCH_2), 3.56 (q, 2H, $^3J_{\text{HH}} = 7.2$ Hz, $\text{COOCH}_2\text{CH}_3$), 3.91 (tt, 1H, $^3J_{\text{HH}} = J_{\text{PH}} = 5.9$ Hz, PCH), 7.28-7.60 (m, 20H, aromatics).

X-ray Crystal Structure Determinations of Complexes 108, 110a, 111, 113a, 114 and 119. Diffraction data were collected at the Nanyang Technological University using a Bruker X8 Apex diffractometer with Mo $K\alpha$ radiation (graphite monochromator). All non-H atoms were refined anisotropically, while Hydrogen atoms were introduced at a fixed distance from the Carbon atoms and were assigned fixed thermal parameters. The absolute configurations of the chiral complexes were determined unambiguously using the Flack parameter.¹¹⁰

Chapter 6

Asymmetric Hydrophosphination of Aldehyde and Imine

6.1 Introduction

The synthesis of functionalized chiral phosphines is considered highly valuable since these ligands play vital roles in metal-catalyzed reactions.¹¹⁵ The asymmetric addition reaction between a P-H moiety and a C-C multiple bond provides a straightforward route to functionized chiral phosphines.¹¹⁶ This transformation can proceed by the assistance of metal-catalysts⁷⁴⁻⁷⁶ or chiral auxiliaries.¹¹⁷ Nevertheless, the number of reports on the addition of the P-H moiety to C=N¹²⁰ or C=O bond is few.^{66,121-123} Recently, enantioselective organocatalytic hydrophosphination of α,β -unsaturated aldehydes have been reported. However, the addition of the P-H moiety takes places chemoselectively to C=C bond but not C=O bond.⁷⁷⁻⁷⁸ On the other hand, hydrophosphination of cinnamaldehyde has been investigated in organic solvent and using neat reagents.^{66,121} Although these reports have showed that hydrophosphination of both C=C and C=O bonds takes place, no chirality is present.

We have previously reported the synthesis of optically pure phosphines *via* chiral metal ion promoted asymmetric hydrophosphination reactions.⁸²⁻⁸⁴ In pursuing our interest in the asymmetric hydrophosphination of aldehydes, we further investigated the preparation of an optically pure alcohol functionalized 1,3-

diphosphine *via* the addition of a P-H moiety to a C=O bond of coordinated 2-(diphenylphosphino)benzaldehyde. The addition of a P-H moiety to a C=N bond of 2-(Diphenylphosphino)-N-phenyl benzamine is also discussed in this chapter.

6.2 Results and Discussion

6.2.1 Hydrophosphination Reaction Between Diphenylphosphine and 2-(Diphenylphosphino)benzaldehyde

It is noteworthy that in the absence of a metal ion, diphenylphosphine shows no reactivity with 2-(diphenylphosphino)benzaldehyde or 2-(Diphenylphosphino)-N-phenyl benzamine under ambient conditions. As illustrated in Scheme 6.1, 2-(diphenylphosphino)benzaldehyde **124** was coordinated to (*R*)-**72** regioselectively to form complex **125**, which upon abstraction of the chloro ligand with silver perchlorate gave the perchlorato complex **126**. The ^{31}P NMR spectrum in CDCl_3 exhibited one single peak at δ 36.4 and 34.2 for complexes **125** and **126** respectively.

Scheme 6.1

Complex **126** was not isolated but was subsequently treated with an equivalent of diphenylphosphine at room temperature for 3 h to yield the desired hydrophosphination products. The ^{31}P NMR spectrum of the crude reaction mixture in CDCl_3 exhibited two pair of doublets at δ 1.0, 66.5 ($J_{\text{PP}} = 54.6$ Hz) and 6.6, 53.5 ($J_{\text{PP}} = 55.6$ Hz) with the relative intensities of 1:6. These signals indicated that two of the four possible isomeric products were generated in the hydrophosphination reaction. Subsequently, the major isomer **127d** was separated by means of column chromatography and fractional crystallization as white needle-like crystals from dichloromethane-diethyl ether in 65% yield. The ^{31}P NMR spectrum of pure **127d** in CDCl_3 showed a pair of doublets at δ 6.6, 53.5 ($J_{\text{PP}} = 55.6$ Hz). The molecular structure and the absolute stereochemistry of **127d** were determined by X-ray crystallography (Fig. 6.1). Selected bond lengths and angles are given in Table 6.1.

Figure 6.1. Molecular structure and absolute stereochemistry of complex **127d**.

Table 6.1. Selected Bond Lengths (Å) and Angles (deg) for **127d**

Pd(1)-C(1)	2.066(9)
Pd(1)-N(1)	2.173(6)
Pd(1)-P(1)	2.386(2)
Pd(1)-P(2)	2.246(2)
P(2)-C(33)	1.893(9)
P(1)-C(27)	1.856(9)
C(27)-C(32)	1.406(13)
C(32)-C(33)	1.504(14)
C(27)-C(28)	1.358(14)
C(28)-C(29)	1.369(14)
C(29)-C(30)	1.386(15)
C(30)-C(31)	1.383(15)
C(31)-C(32)	1.402(12)
C(1)-Pd(1)-N(1)	81.0(3)
P(2)-Pd(1)-N(1)	171.68(18)
C(1)-Pd(1)-P(1)	173.7(3)
P(2)-Pd(1)-P(1)	90.41(7)
N(1)-Pd(1)-P(1)	97.89(18)
C(1)-Pd(1)-P(2)	90.8(2)
Pd(1)-P(2)-C(33)	112.4(3)
Pd(1)-P(1)-C(27)	115.5(3)
P(1)-C(27)-C(32)	119.3(7)
P(2)-C(33)-C(32)	111.0(7)
C(33)-C(32)-C(27)	123.4(8)

As shown in Scheme 6.2, the (*R*)-naphthylamine auxiliary can be chemoselectively removed from **127d** by treatment with concentrated hydrochloric acid to give the dichloride **128** as yellowish crystals from dichloromethane and

diethyl ether in 90% isolated yield. The ^{31}P NMR spectrum of the dichloro complex in CDCl_3 showed two broad singlets: δ 17.0, 65.9. The molecular structure and the absolute stereochemistry of **128** were determined by X-ray crystallography. Two different conformational structures were detected (Fig. 6.2 and 6.3). Selected bond lengths and angles are given in Table 6.2 and 6.3.

Scheme 6.2

Figure 6.2. Molecular structure and absolute stereochemistry of complex **128a**.

Table 6.2. Selected Bond Lengths (Å) and Angles (deg) for **128a**

Pd(1)-Cl(1)	2.3508(16)
Pd(1)-Cl(2)	2.3654(16)
Pd(1)-P(1)	2.2574(15)
Pd(1)-P(2)	2.2339(16)
P(2)-C(19)	1.866(6)
P(1)-C(13)	1.824(5)
C(13)-C(18)	1.414(8)
C(18)-C(19)	1.509(8)
Cl(1)-Pd(1)-Cl(2)	90.45(6)
P(2)-Pd(1)-Cl(2)	86.41(6)
Cl(1)-Pd(1)-P(1)	92.19(6)
P(2)-Pd(1)-P(1)	91.67(6)
Cl(2)-Pd(1)-P(1)	170.19(6)
Cl(1)-Pd(1)-P(2)	174.36(5)
Pd(1)-P(2)-C(19)	115.33(19)
Pd(1)-P(1)-C(13)	113.75(18)
P(1)-C(13)-C(18)	122.4(4)
P(2)-C(19)-C(18)	108.4(4)
C(19)-C(18)-C(13)	121.8(5)

Figure 6.3. Molecular structure and absolute stereochemistry of complex **128b**.

Table 6.3. Selected Bond Lengths (Å) and Angles (deg) for **128b**

Pd(2)-Cl(3)	2.3591(17)
Pd(2)-Cl(4)	2.3581(16)
Pd(2)-P(3)	2.2626(16)
Pd(2)-P(4)	2.2301(16)
P(4)-C(50)	1.848(7)
P(3)-C(44)	1.834(6)
C(44)-C(49)	1.405(7)
C(49)-C(50)	1.489(9)
Cl(3)-Pd(2)-Cl(4)	92.20(6)
P(4)-Pd(2)-Cl(4)	85.21(6)
Cl(3)-Pd(2)-P(3)	91.35(6)

P(4)-Pd(2)-P(3)	92.86(6)
Cl(4)-Pd(2)-P(3)	166.06(6)
Cl(3)-Pd(2)-P(4)	172.38(6)
Pd(2)-P(4)-C(50)	110.9(2)
Pd(2)-P(3)-C(44)	112.7(2)
P(3)-C(44)-C(49)	120.8(4)
P(4)-C(50)-C(49)	109.1(4)
C(50)-C(49)-C(44)	121.4(5)

6.2.2 Hydrophosphination Reaction Between Diphenylphosphine and

2-(Diphenylphosphino)-N-phenyl benzamine

2-(Diphenylphosphino)-N-phenyl benzamine **129** was prepared from 2-(diphenylphosphino)benzaldehyde **124** according to standard literature method as shown in Scheme 6.3.¹²⁴ The ³¹P NMR spectrum in CDCl₃ exhibited one single peak at δ -11.0 and -12.6 for phosphines **124** and **129** respectively.

Scheme 6.3

As illustrated in Scheme 6.4, 2-(Diphenylphosphino)-N-phenyl benzamine **129** was coordinated to (*R*)-**72** regioselectively to form complex **130**, which upon abstraction of the chloro ligand with silver perchlorate gave the perchlorato complex **131**. The ³¹P NMR spectrum in CDCl₃ exhibited one single peak at δ 36.9 and 37.1 for complexes **130** and **131** respectively.

Scheme 6.4

Complex **131** was not isolated but was subsequently treated with an equivalent of diphenylphosphine at room temperature for 2 d to yield the desired hydrophosphination products. The ^{31}P NMR spectrum of the crude reaction mixture in CDCl_3 exhibited four pair of doublets at δ 4.0, 62.6 ($J_{\text{PP}} = 52.0$ Hz), 4.7, 53.3 ($J_{\text{PP}} = 56.3$ Hz), 29.8, 46.2 ($J_{\text{PP}} = 50.2$ Hz) and 7.8, 42.4 ($J_{\text{PP}} = 50.8$ Hz) with the relative intensities of 2:6:1:1. These signals indicated that four possible isomeric products were generated in the hydrophosphination reaction. The cationic diastereomers could not be separated efficiently by chromatography or fractional crystallization. The diastereomeric mixture was then treated with concentrated hydrochloric acid to remove the naphthylamine auxiliary resulting in the dichloro complexes **133a** and **133b**. Crystallization of the reaction mixture from dichloromethane and diethyl ether gave the racemic dichloro complex **133** as

yellow crystals (40% yield). The ^{31}P NMR spectrum of pure **133** in CDCl_3 showed two broad singlets at δ 19.0, 67.2. The molecular structure and the absolute stereochemistry of **133** were determined by X-ray crystallography (Fig. 6.4). Selected bond lengths and angles are given in Table 6.4.

Figure 6.4. Molecular structure and absolute stereochemistry of complex **133**.

Table 6.4. Selected Bond Lengths (Å) and Angles (deg) for **133**

Pd(1)-Cl(1)	2.3306(8)
Pd(1)-Cl(2)	2.3706(8)
Pd(1)-P(1)	2.2459(8)
Pd(1)-P(2)	2.2598(8)
P(2)-C(25)	1.818(3)
P(1)-C(13)	1.848(3)

C(13)-C(20)	1.513(4)
C(20)-C(25)	1.415(4)
N(1)-C(13)	1.446(4)
N(1)-C(14)	1.402(8)
C(20)-C(21)	1.386(4)
C(21)-C(22)	1.390(5)
C(22)-C(23)	1.379(5)
C(23)-C(24)	1.383(4)
C(24)-C(25)	1.392(4)
Cl(1)-Pd(1)-Cl(2)	91.33(3)
P(2)-Pd(1)-Cl(2)	87.04(3)
Cl(1)-Pd(1)-P(1)	89.14(3)
P(2)-Pd(1)-P(1)	92.49(3)
Cl(2)-Pd(1)-P(1)	175.22(3)
Cl(1)-Pd(1)-P(2)	178.37(3)
Pd(1)-P(2)-C(25)	117.24(10)
Pd(1)-P(1)-C(13)	111.04(11)
P(1)-C(13)-C(20)	110.3(2)
P(2)-C(25)-C(20)	122.6(2)
C(25)-C(20)-C(13)	123.0(3)
C(20)-C(13)-N(1)	116.6(3)
P(1)-C(13)-N(1)	107.3(2)
C(13)-N(1)-C(14)	122.5(5)

6.3 Conclusion

In conclusion, the asymmetric hydrophosphination reactions of diphenylphosphine and 2-(diphenylphosphino)-benzaldehyde or 2-(Diphenylphosphino)-N-phenyl benzamine promoted by an organopalladium(II) complex derived from (*R*)-N,N-dimethyl-1-(1-naphthyl)-ethylamine as the chiral auxiliary proceeded in high regio- and stereoselectivities under mild conditions. The naphthylamine auxiliaries were removed chemoselectively from the addition products by treatment with concentrated hydrochloric acid to form the di-chloro complexes.

6.4 Experimental Section

Reactions involving air-sensitive compounds were performed under a positive pressure of purified 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 0.1dm cell at 25 °C with a Perkin-Elmer model 341 polarimeter. Elemental analyses were performed by the staff in the Elemental Analysis Laboratory of the Division of Chemical and Biological Chemistry of Nanyang Technological University. Melting points were measured using the SRS Optimelt Automated Melting Point System, SRS MPA100.

All solvents used for the synthesis of ligands and reactions were deoxygenated using a positive pressure of argon. Analytical-grade chemicals were purchased from Sigma-Aldrich and Strem Chemicals. 2-(Diphenylphosphino)-N-phenyl benzamine was prepared according to standard literature method.¹²⁴

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

Hydrophosphination of [(R)-Chloro[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-C,N]][(2-(diphenylphosphino)benzaldehyde-P]palladium(II), 125.

Synthesis of Complex 127d. A mixture of (R)-72 (0.585 g) and 2-(diphenylphosphino)benzaldehyde (0.500 g) was stirred in dichloromethane (50 mL) at room temperature for 2 h. Aqueous silver perchlorate (0.700 g) was added into the solution and the reaction mixture was stirred vigorously at room temperature for 2 h. The mixture was filtered through Celite, washed with water (3 X 30 mL) and dried with MgSO₄. The mixture was then degassed and treated with diphenylphosphine (0.320 g) at room temperature for 3 h. The crude product was recrystallized from dichloromethane and diethyl ether to give **127d** as yellow crystals, 1.128 g (65% yield). ³¹P NMR (CDCl₃) δ 6.6, 53.5 (*J*_{PP} = 55.6 Hz); ¹H NMR (CDCl₃) δ 1.91 (s, 3H, *NMe_{eq}*), 2.20 (d, 3H, *CHMe*, ³*J*_{HH} = 6.0 Hz), 2.64 (s, 3H, *NMe_{ax}*), 4.41 (qn, 1H, ³*J*_{HH} = ⁴*J*_{PH} = 6.0 Hz, *CHMe*), 4.59 (dd, 1H, ³*J*_{HH} = 3.9 Hz, ³*J*_{PH} = 23.8 Hz, *PCHOH*), 5.72 (dd, 1H, ³*J*_{HH} = 3.9 Hz, ²*J*_{PH} = 7.6 Hz, *PCH*), 6.98-8.11 (m, 30H, aromatics).

Synthesis of Complex 128. Concentrate hydrochloric acid (10 mL) was added to a solution of **127d** (0.30 g) in dichloromethane (25 mL). The reaction mixture was stirred vigorously at room temperature for 12 h, washed with water (3 × 20 mL)

and dried (magnesium sulfate). Crystallization of the crude product from acetonitrile and diethyl ether gave the dichloro complex as yellowish crystals: 0.175 g (90% yield). ^{31}P NMR (CDCl_3) δ 17.0, 65.9; ^1H NMR (CDCl_3) δ 2.71 (b, 1H, PCHOH), 5.85 (d, 1H, $^2J_{\text{PH}} = 7.6$ Hz, PCH), 6.69-8.12 (m, 24H, aromatics).

Hydrophosphination of [(*R*)-Chloro[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*][(2-(diphenylphosphino)-*N*-phenyl benzamine-*P*)] palladium (II), 130. Synthesis of Complex 133. A mixture of (*R*)-**72** (0.486 g) and 2-(diphenylphosphino)-*N*-phenyl benzamine (0.523 g) was stirred in dichloromethane (50 mL) at room temperature for 2 h. Aqueous silver perchlorate (0.700 g) was added into the solution and the reaction mixture was stirred vigorously at room temperature for 2 h. The mixture was filtered through Celite, washed with water (3 X 40 mL) and dried with MgSO_4 . The mixture was then degassed and treated with diphenylphosphine (0.202 g) at room temperature for 24 h. Concentrate hydrochloric acid (10 mL) was added to the solution. The reaction mixture was stirred vigorously at room temperature for 12 h, washed with water (3 X 40 mL) and dried (magnesium sulfate). Crystallization of the crude product from acetonitrile and diethyl ether gave the dichloro complex **133** as yellow crystals: 0.454 g (40% yield). ^{31}P NMR (CDCl_3) δ 19.0, 67.2; ^1H NMR (CDCl_3) δ 3.93 (b, 1H, PCHNH), 5.86 (d, 1H, $^2J_{\text{PH}} = 7.7$ Hz, PCH), 6.62-8.12 (m, 29H, aromatics).

X-ray Crystal Structure Determinations of Complexes 127d, 128a, 128b and 133. Diffraction data were collected at the Nanyang Technological University

using a Bruker X8 Apex diffractometer with Mo K α radiation (graphite monochromator). All non-H atoms were refined anisotropically, while Hydrogen atoms were introduced at a fixed distance from the Carbon atoms and were assigned fixed thermal parameters. The absolute configurations of the chiral complexes were determined unambiguously using the Flack parameter.¹¹⁰

Chapter 7

Chiral Palladium Template Promoted Asymmetric Synthesis of Bisphosphine Monoxide Ligand

7.1 Introduction

Bisphosphine monoxides have proven to be successful hemilabile ligands for hydroformylation,⁸⁵ carbonylation⁸⁶ and other reactions.⁸⁷ Due to the presence of both the soft (P) and hard (O) nucleophilic centers on one heterobidentate ligand, bisphosphine monoxides show unique coordination, stabilization and chelating properties which make them quite useful in organometallic synthesis and catalysis.⁸⁸ However, optically pure bisphosphine monoxides are relatively rare and most of them are obtained from existing chiral bisphosphines *via* selective oxidation reactions.⁹⁰ The synthesis of chiral bisphosphine monoxide ligands *via* addition reactions from easily accessible non-chiral bisphosphines is much less developed.

Over the past few years, our group has reported the use of chiral cyclometalated-amine complexes as efficient promoters for asymmetric synthesis of chiral phosphines by means of Diels–Alder reactions,⁹¹ hydroamination reactions,⁹² hydrophosphination reactions⁸²⁻⁸⁴ and hydroarsination reactions.⁹³ Asymmetric oxidation of polyphosphines has also been studied.⁷¹ This chapter describes two synthetic pathways towards a chiral bisphosphine monoxide *via* the hydroalkoxylation reaction and the selective oxidation reaction.

7.2 Results and Discussion

It is well known that the vinylidene double bond of 1,1-bis(diphenylphosphino)ethylene **134** is activated towards a series of addition reactions when the diphosphine is coordinated to transition metals. However, their addition products are not chiral upon liberation from the metal templates due to the existence of two symmetric phosphorus atoms. It is expected therefore that selective oxidation of one of the two phosphorus atoms can make the 1,1-bis(diphenylphosphino)ethylene a prochiral molecule and the subsequent addition products should be chiral. Hence 1,1-bis(diphenylphosphino)ethylene monoxide **135** was prepared *via* direct oxidation. As shown in Scheme 7.1, a solution of 1,1-bis(diphenylphosphino)ethylene and one equivalent of hydrogen peroxide were stirred in dichloromethane for 2 hours followed by column chromatography. The reaction gave a mixture of unreacted 1,1-bis(diphenylphosphino)ethylene, the monoxide **135**, and the dioxide. The monoxide 1,1-bis(diphenylphosphino)-ethane monoxide **135** was isolated as yellowish solid in 52% yield and 15% of 1,1-bis(diphenylphosphino)ethylene was recovered. The ^{31}P NMR spectrum of **135** in CDCl_3 exhibited a pair of doublet resonance signals at δ -12.2, 29.0 ($J_{\text{PP}} = 83.5$ Hz). It is noteworthy that addition of different quantity of hydrogen peroxide resulted in lower yield of the target 1,1-bis(diphenylphosphino)ethylene monoxide.

Scheme 7.1

In this approach, as illustrated in Scheme 7.1, 1,1-bis(diphenylphosphino)ethylene monoxide **135** was coordinated to complex (*R*)-**79** regioselectively to form the neutral complex (*R*)-**138** in 99% yield. The ^{31}P NMR spectrum of the crude product in CDCl_3 exhibited only one pair of doublets resonance signals at δ 35.7, 49.3 ($J_{\text{PP}} = 64.4$ Hz). The coordination product (*R*)-**138** was not routinely isolated but was generally treated directly with other reactants. However, in order to determine its molecular structure and the coordination chemistry, some samples of (*R*)-**138** were crystallized from dichloromethane-diethyl ether in quantitative yield and analyzed by X-ray crystallography, $[\alpha]_{\text{D}} +22$ (c 0.5, CH_2Cl_2) (Figure 7.1). Selected bond lengths and angles are given in Table 1. The structural analysis affirmed that the newly formed five-membered chelate ring has the asymmetric skew conformation of λ helicity, and the soft donor P atom takes up the expected coordination position *trans* to the NMe_2 moiety while the hard donor O atom is *trans* to the naphthalene carbon.

Figure 7.1. Molecular structure and absolute stereochemistry of (*R*)-**138**.

Table 7.1. Selected Bond Lengths (Å) and Angles (deg) for (*R*)-**138**

Pd(2)-Cl(3)	2.3591(17)
Pd(2)-Cl(4)	2.3581(16)
Pd(2)-P(3)	2.2626(16)
Pd(2)-P(4)	2.2301(16)
P(4)-C(50)	1.848(7)
P(3)-C(44)	1.834(6)
C(44)-C(49)	1.405(7)
C(49)-C(50)	1.489(9)
Cl(3)-Pd(2)-Cl(4)	92.20(6)
C(1)-Pd(1)-O(1)	172.28(11)
P(2)-Pd(1)-O(1)	89.31(6)
N(1)-Pd(1)-O(1)	90.87(9)

C(1)-Pd(1)- P(2)	98.37(9)
Pd(1)- P(2)-C(27)	102.79(10)
Pd(1)-O(1)-P(1)	115.55(11)
O(1)-P(1)-C(27)	107.54(13)
P(2)-C(27)-P(1)	108.79(15)

Coordination product (*R*)-**138** was subsequently treated with methanol in benzene. In the absence of any external base, methanol shows no reactivity with (*R*)-**138** under ambient conditions. However, upon addition of one equivalent of triethyl amine, the hydroalkoxylation reaction proceeds smoothly at room temperature. The reaction was monitored by the ^{31}P NMR spectroscopy and was found to be complete in 6 hours to give a 4:1 mixture of diastereomers **139a** and **139b** in 95% conversion yield. The ^{31}P NMR spectrum of the crude product exhibited two pairs of doublets resonance signals at δ 43.8, 58.6 ($J_{\text{PP}} = 30.0$ Hz) (**139a**) and 42.9, 58.0 ($J_{\text{PP}} = 25.1$ Hz) (**139b**). The stereoselectivity of the hydroalkoxylation reaction is not affected by the excess amount of triethyl amine. However, the reaction is influenced by solvent effects. When the reaction was performed in various solvents such as ethyl acetate, dichloromethane, acetone, tetrahydrofuran, acetonitrile and methanol, it gave lower conversion yields and the ratios of **139a** to **139b** obtained were 4.3:1, 2.8:1, 2.8:1, 2.8:1, 2.5:1 and 3:1, respectively. It is noteworthy that the adducts **139a** and **139b** were interconvertible. However, this process took quite a long time and only occurred in solution in the presence of external base. The major isomer **139a** was obtained from dichloromethane and diethyl ether as colorless crystals, 0.623 g (60% yield): $[\alpha]_{\text{D}}^{+14}$ (*c* 0.5, CH_2Cl_2). Unfortunately, single crystals of the complex **139a** that are

suitable for X-ray structural investigation could not be produced. Accordingly, it was necessary to determine the absolute stereochemistry of complex **139a** by the 2D rotating frame nuclear Overhauser enhancement (ROESY) ^1H NMR technique. We have previously applied this reliable 2D NMR technique for the assignments of the absolute stereochemistry in a series of coordinated chiral phosphines containing the same orthometalated naphthylamine auxiliary.

Figure 7.2 Numbering scheme of complex **139a** for the ROESY NMR studies.

Assignment of Absolute Stereochemistry of addition product. Figure 7.2 shows the numbering scheme of the complex **139a** used in the 2D ROESY NMR analysis. In these NMR analyses, the well-established stereochemical features of the orthometalated (*R*)-naphthylamine unit within the complex **139a** are used as the internal stereochemical references. Due to the repulsive interaction between Me(11) and the proximal H(8) naphthylene proton, Me(11) invariably takes up the axial position in the stable five-membered organopalladium ring which adopts the static δ absolute conformation. On the other hand, the prochiral N-Me groups attached to the organopalladium ring are locked by the rigid δ ring conformation into the nonequivalent axial and equatorial positions. The axial NMe group projects perpendicularly below the palladium centered square-plane, while the equatorial NMe group protrudes somewhat above the plane and towards the adjacent oxygen

donor in the O-P ring. With reference to the unique structural feature of the auxiliary, appropriate interchelate NOE interactions between the naphthylamine auxiliary and the diphosphines monoxide chelate would allow the assignment of the absolute stereochemistry of complex **139a**.

Selected ^{31}P and ^1H NMR data of complex **139a** are given in Table 7.2. These NMR assignments are based on a series of ^{31}P and ^1H and 2D ^1H -ROESY NMR studies of complex **139a**. Figure 3 shows the 2D ^1H - ^1H ROESY NMR spectra of the major addition product **139a**. In this spectra, the characteristic NOE patterns within the orthometalated (*R*)-naphthylamine ring are clearly record. For example, the driving forces for Me(11) to assume the axial position, i.e., the H(8)-Me(11) (A) and H(8)-H(11) (M) repulsive interactions, are clearly reflected in the spectrum. Strong NOE signals (B), (G), (H) are observed for the expected proximities between H(11) and three methyl groups Me(11), NMe(ax), NMe(eq) respectively. Signal (C) represent the NOE interaction between Me(11) and NMe(eq) while no interaction between Me(11) and NMe(ax) is observed.

Table 7.2. Selected ^1H NMR Spectra Chemical Shift Values of **139a** in CDCl_3 .

CHMe	2.12	CH ₂ OMe	3.40
CH ₂ OMe	2.79	CHMe	4.58
NMe(ax)	3.06	PCHCH ₂	4.70
NMe(eq)	3.16		

In Figure 7.3, the 2D ROESY NMR spectrum of **139a** shows long-range interchelate NOE interactions between Me(18) and Me(11) (signal D), Me(18) and

NMe(eq) (signal E). Furthermore, NOE signal (I) is observed between H(15) and NMe(eq). No interaction between NMe(ax) and H(15), or NMe(ax) and Me(18) is observed. These NOE signals thus indicate that Me(18) is located on the same side above the square plane with Me(11) and NMe(eq). Accordingly, the absolute configuration at the new-formed carbon center is *R*.

Figure 7.3 Two-dimensional ^1H ROESY NMR spectrum of complex **139a** in CDCl_3 . All off-diagonal peaks are of negative intensity. Selected NOE contacts: A,

H8-Me11; B, H11-Me11; C, Me11-Me12(eq); D, Me11-Me18; E, Me12(eq)-Me18; F, H17-Me18; G, H11-Me12(eq); H, H11-Me12(ax); I, H15-Me12(eq); J, H15-H17; K, H17-Ph; L, H11-Ph; M, H11-Ph'; N, H15-Ph; O, H15-Ph'.

Selective Oxidation of Coordinated Bisphosphines

As shown in Scheme 7.1, another synthetic pathway towards **139a** and **139b** is the selective oxidation of coordinated biphosphines in the hydroalkoxylation products **137a** and **137b**. In this approach, the diphosphine 1,1-bis(diphenylphosphino)-ethane **134** was coordinated to chiral palladium template (*R*)-**79** to form the neutral complex (*R*)-**136**. The ^{31}P NMR spectrum of the crude product in CDCl_3 exhibited a pair of doublet resonance signals at δ -4.4, 13.6 ($J_{\text{PP}} = 25.1$ Hz). The coordination product (*R*)-**136** was subsequently treated with methanol and 30% equivalent of triethylamine in dichloromethane at room temperature for 1.5h, giving the desired hydroalkoxylation products **137a** and **137b** in 96% yield. In the absence of triethylamine, only 82% conversion was observed even longer reaction time was allowed. The ^{31}P NMR spectrum of the crude products exhibited two pairs of doublet resonance signals at δ -17.5, 8.4 ($J_{\text{PP}} = 47.6$ Hz) and -20.5, 7.9 ($J_{\text{PP}} = 49.4$ Hz) with the ratio 1.5:1. The cationic diastereomers **137a** and **137b** could not be separated efficiently by chromatography or fractional crystallization. The diastereomeric mixture in dichloromethane was subsequently treated with two equivalents of hydrogen peroxide subsequently. The stereoselectivity of the oxidation reaction is affected by external base. Without NEt_3 , only 5% of **137a,b** were transformed into **139a,b** in dichloromethane or

methanol at room temperature in 24h. The ^{31}P NMR spectroscopy was used to monitor the reaction and exhibited two new pairs of doublet resonance signals at δ 43.8, 58.6 ($J_{\text{PP}} = 30.0$ Hz) (**139a**) and 42.9, 58.0 ($J_{\text{PP}} = 25.1$ Hz) (**139b**) with the ratio 1:1.2. In this process, no other products were formed and the oxidation reaction only occurred at the phosphorus center which *trans* to the naphthalene carbon. When the reaction was performed at 40 °C under similar conditions, *ca.* 50-60% of **137a,b** were converted into **139a,b** in the same ratio. There were also the coordination product (*R*)-**138** and few minor unidentified species.

With excess equivalent of NEt₃ (1.2 equiv.), 60% of **137a,b** were converted into **139a,b** in dichloromethane or methanol respectively at room temperature in 24h. The ^{31}P NMR spectrum found two new pairs of doublet resonance signals at δ 43.8, 58.6 ($J_{\text{PP}} = 30.0$ Hz) (**139a**) and 42.9, 58.0 ($J_{\text{PP}} = 25.1$ Hz) (**139b**) with the 3:1 ratio. The major difference in these two solvent systems is that, when the reaction was performed in dichloromethane, (*R*)-**138** was obtained in 20% yield while the product could not be obtained in methanol. In addition, the ratio of **139a** to **139b** in this reaction is consistent with that of the hydroalkoxylation reaction of (*R*)-**138** (when it was performed in methanol). From the discussion above, we believe that with triethylamine functioned as an external base. The reaction rate of **137a,b** to (*R*)-**138** is faster than the direct conversion rate of **137a,b** to **139a,b**. When (*R*)-**138** was formed in the reaction, it subsequently underwent hydroalkoxylation reaction and was converted into **139a,b**. If the reaction was performed in pure dichloromethane, the amount of methanol in reaction mixture was not sufficient enough to initiate the addition reaction.

Free Ligand Liberation

The bis-phosphine monoxide ligand in **139a** could be rapidly displaced from the chiral palladium template by the strong chelating agent diphenylphosphino ethane (dppe) as shown in Scheme 7.2. The corresponding optically active ligand **140a** was liberated with formation of complex **141**. The reaction mixture was passed through a column of Florisil using dichloromethane to yield a colorless solution. Removal of solvent under reduced pressure gave **140a** as white solid with 75% yield, $[\alpha]_D +56.7$ (c 0.5, CH_2Cl_2). The ^{31}P NMR spectrum of bisphosphine monoxide **140a** exhibited a pair of doublet resonance signals at δ -15.2, 33.7 ($J_{\text{PP}} = 67.0$ Hz).

Scheme 7.2

As illustrated in Scheme 7.3, the optical purity of **140a** was confirmed by the quantitative reparation of **139a** from the liberated ligand and (*R*)-**79**; The ^{31}P NMR spectrum of the crude product in CDCl_3 exhibited only a pair of doublet signals at δ 43.8, 58.6 ($J_{\text{PP}} = 30.0$ Hz). These signals are identical to those recorded for the major diastereomer **139a** generated directly from original reaction. As a further test of the optical purity of the liberated ligand and to confirm the identity of the minor product, **140a** was recomplexed to the equally accessible (*R*)-**79**. The ^{31}P NMR spectrum of the crude recomplexation product in CDCl_3 exhibited only a

pair of doublet signals at δ 42.9, 58.0 ($J_{\text{PP}} = 25.1$ Hz). These signals were identical with those observed for the minor product **139b**. Hence, it could be confirmed that **139b** was indeed the minor product of the original asymmetric synthesis and the liberated bis-phosphine monoxide **140a** is indeed optically pure.

Scheme 7.3

7.3 Conclusion

In conclusion, two converging synthetic pathways sharing a common metal template promoted asymmetric hydroalkoxylation and oxidation process have been illustrated for the synthesis of chiral bis-phosphine monoxide ligands. The asymmetric hydroalkoxylation of coordinated non-chiral bis-phosphine monoxide proved to be a more effective synthetic process than the other one.

7.4 Experimental Section

Reactions involving air-sensitive compounds were performed under a positive pressure of purified 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 0.1dm cell at 25 °C with a Perkin-Elmer model 341 polarimeter. Elemental analyses were performed by the staff in the Elemental Analysis

Laboratory of the Division of Chemical and Biological Chemistry of Nanyang Technological University. Melting points were measured using the SRS Optimelt Automated Melting Point System, SRS MPA100.

All solvents used for the 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(acetonitrile) [(*S*)-1-[1-(dimethylamino)ethyl]-2-phenyl-*C*, *N*]-palladium(II) perchlorate ((*R*)-**79**)^{94a, 108} 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 cyanide compounds.

Synthesis of 1,1-bis(diphenylphosphino)-ethylene monoxide, 135. A mixture of 1,1-bis(diphenylphosphino)ethylene (1.982 g) and hydrogen peroxide (0.170 g) in dichloromethane (80 mL) was stirred at room temperature for 2 h. The solvent was removed under reduced pressure. This material was chromatographed on a silica gel column with ethyl acetate-dichloromethane (1:3 v/v) as the eluent, giving the bisphosphine monoxide **135** as yellowish solid: 1.072 g (52% yield). Mp 112–113 °C. Anal. Calcd. for C₂₆H₂₂P₂O: C, 75.7; H, 5.4. Found: C, 75.3; H, 5.6. ³¹P NMR (CDCl₃) δ -12.2, 29.0 (*J*_{PP} = 83.5 Hz); ¹H NMR (CDCl₃) δ 6.06 (ddd, 1H, CHH', ²*J*_{H'H} = 1.3 Hz, *J*_{P'H} = 39.6 Hz, *J*_{PH} = 8.0 Hz), 6.96 (ddd, 1H, CHH', ²*J*_{HH'} = 1.3 Hz, *J*_{PH'} = 22.3 Hz, *J*_{P'H'} = 11.6 Hz), 7.19–7.76 (m, 20H, aromatics).

Synthesis of [(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-*C,N*]{1,1-bis(diphenyl-phosphino)-ethylene monoxide-*P,O*}-palladium (II) Perchlorate, (*R*)-138. A mixture of 1-bis(diphenylphosphino)ethane monoxide **135** (0.843 g) and (*R*)-79 (0.994 g) in dichloromethane (60 mL) was stirred at room temperature for 2h. After removal of the organic solvent, the complex (*R*)-138 was isolated as yellow solid, 1.837 g (99% yield). $[\alpha]_D^{+22}$ (*c* 0.5, CH₂Cl₂); Mp 158 °C (dec.). Anal. Calcd. for C₄₀H₃₈ClNO₅P₂Pd: C, 58.8; H, 4.7; N, 1.7. Found: C, 58.3; H, 4.7; N, 1.4. ³¹P NMR (CDCl₃) δ 35.7, 49.3 (*J*_{PP} = 64.4 Hz); ¹H NMR (CDCl₃) δ 1.88 (d, 3H, CHMe, ³*J*_{HH} = 6.2 Hz), 2.94 (s, 6H, NMe₂), 4.48 (qn, 1H, ³*J*_{HH} = ⁴*J*_{PH} = 6.2 Hz, CHMe), 6.28-6.44 (m, 2H, CCH₂), 6.89-7.78 (m, 26H, aromatics).

Hydroalkoxylation Reaction. Isolation of 139a. A mixture of (*R*)-138 (1.000 g), triethylamine (0.124 g) and methanol (2 mL) was stirred in benzene (50 mL) at room temperature for 6 h. The solvent was removed and complex **139a** was obtained from dichloromethane and diethyl ether as colorless crystals, 0.623 g (60% yield). $[\alpha]_D^{+14}$ (*c* 0.5, CH₂Cl₂); Mp 195 °C (dec.). Anal. Calcd. for C₄₁H₄₂ClNO₆P₂Pd: C, 58.0; H, 5.0; N, 1.7. Found: C, 57.4; H, 5.1; N, 1.6. ³¹P NMR (CDCl₃) δ 43.8, 58.6 (*J*_{PP} = 30 Hz); ¹H NMR (CDCl₃) δ 2.12 (d, 3H, CHMe, ³*J*_{HH} = 6.2 Hz), 2.79 (s, 3H, OMe), 3.06 (s, 3H, NMe_{eq}), 3.16 (d, 3H, *J*_{PH} = 3.2 Hz, NMe_{ax}), 3.24-3.43 (m, 2H, CH₂OMe), 4.58 (qn, 1H, ³*J*_{HH} = ⁴*J*_{PH} = 6.2 Hz, CHMe), 4.65-4.76 (m, 1H, CHCH₂OMe), 6.57-8.39 (m, 26H, aromatics).

Synthesis of Bis-phosphine Monoxide 140a. A mixture of **139a** (0.103 g) and diphenylphosphino ethane (0.048 g) was stirred in dichloromethane at room temperature for 15 min. The resulting yellowish mixture was passed through a chromatography column using dichloromethane-acetone as eluent. Removal of solvent under reduced pressure gave **140a** as air-sensitive yellowish solid, 0.040 g (75% yield), $[\alpha]_D +40.9$ (c 0.1, CH_2Cl_2). ^{31}P NMR (CDCl_3) δ -15.2, 33.7 ($J_{\text{PP}} = 67.0$ Hz); ^1H NMR (CDCl_3) δ 2.69 (s, 3H, OMe), 3.36-3.47 (m, 2H, CH_2OMe), 5.30-5.32 (m, 1H, CHCH_2OMe), 7.29-7.80 (m, 20H, aromatics).

X-ray Crystal Structure Determinations of Complexes (*R*)-138.

Diffraction data were collected at the Nanyang Technological University using a Bruker X8 Apex diffractometer with Mo $\text{K}\alpha$ radiation (graphite monochromator). All non-H atoms were refined anisotropically, while Hydrogen atoms were introduced at a fixed distance from the Carbon atoms and were assigned fixed thermal parameters. The absolute configurations of the chiral complexes were determined unambiguously using the Flack parameter.¹¹⁰

Conclusion

This thesis investigates the application of the chiral palladium(II) complexes derived from (*S*)- or (*R*)-*N,N*-dimethyl-1-(1-naphthyl)-ethylamine as the chiral auxiliaries in stoichiometric reactions to prepare enantiomerically pure phosphine ligands. There is an internal steric repulsion between the methyl substituent on the stereogenic carbon of the chiral naphthylamine chelate ring and the neighboring naphthylene proton. The crystallographic determinations and rotating Overhauser effect (ROESY) NMR investigations confirmed that the organometallic rings of the chiral palladium(II) complexes are locked into their static conformations, both in the solid state and in solution. Thus the prochiral NMe groups are fixed into the nonequivalent axial and equatorial positions and thus control the stereochemistry of the neighboring coordination sites.

The application of the chiral palladium(II) complexes as resolving agents is demonstrated (chapter 2). Through the interconversion of cationic diastereomeric mixtures from metal complexation of racemic ligand and the chiral palladium(II) complexes, the optically active diphosphine was obtained in high yield.

Chiral palladium(II) complex promoted asymmetric hydrophosphination reactions between diphenylphosphine and functionalized alkenes (chapters 3 and 4), alkynes (chapter 5), aldehyde (chapter 6) and imine (chapter 6) are thoroughly investigated. The addition reactions of P-H moiety to C-C multiple bonds, C=O

bond and C=N bond proceeded in high regio- and stereoselectivity under mild conditions. Triethyl amine was used in some reactions as external base. Generally, the hydrophosphination products were separated by fractional crystallization. The naphthylamine auxiliaries could be removed chemoselectively by treatment with concentrated hydrochloric acid to form the corresponding optically pure neutral dichloro complexes. Subsequently, the dichloro complexes underwent ligand displacement with aqueous cyanide to generate the optically pure diphosphine ligands in high yields.

In pursuing our interest in the synthesis of P-stereogenic phosphines with selected functionalities, asymmetric hydrophosphination reactions between diphenylphosphine and phenyldi[(*Z*)-prop-1-enyl]phosphine or phenyldi[(*E*)-prop-1-enyl]phosphine are discussed (chapter 4). Optically pure diphosphine ligands containing both phosphorus and carbon stereogenic centers were obtained in high yields. Another approach by changing diphenylphosphine to methylphenylphosphine is also investigated in some chapters.

Chiral palladium(II) complex promoted hydroalkoxylation and oxidation reactions are also studied in this thesis (chapter 7). The reactions proceeded in high regio- and stereoselectivity under mild conditions, generating chiral bis-phosphine monoxide in good yield.

In conclusion, the application of the chiral palladium(II) complexes derived from (*S*)- or (*R*)-N,N-dimethyl-1-(1-naphthyl)-ethylamine as resolving reagents and chiral auxiliaries for asymmetric hydrophosphination, hydroalkoxylation and oxidation reactions is demonstrated. Optically active diphosphine ligands with

carbon stereogenic center(s), diphosphine ligands containing both phosphorus and carbon stereogenic centers and chiral bis-phosphine monoxides were obtained in high yields.

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Appendix

X-ray Crystallographic Data

The X-ray structural analyses were kindly performed by Dr. Yongxin Li at Division of Chemistry and Biological Chemistry, Nanyang Technological University. Complete tables of crystal data, data collection, solution and refinement, final positional parameters, bond distances and angles, thermal parameters of non-hydrogen atoms and calculated hydrogen parameters are available from Professor Leung Pak Hing upon request.

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

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

Table A1 Crystallographic Data for Complex (**S**)-85

Empirical formula	$C_{20}H_{26}ClN_3O_4Pd$
Formula weight	514.29
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)
Unit cell dimensions	$a = 12.0920(5)$ Å $\alpha = 90^\circ$. $b = 7.4604(4)$ Å $\beta = 104.924(2)^\circ$. $c = 13.3336(6)$ Å $\gamma = 90^\circ$.
Volume	$1162.27(9)$ Å ³
Z	2
Density (calculated)	1.470 Mg/m ³
Absorption coefficient	0.942 mm ⁻¹
F(000)	524
Crystal size	0.30 x 0.24 x 0.14 mm ³
Theta range for data collection	1.58 to 30.57°.
Index ranges	-17<= <i>h</i> <=17, -8<= <i>k</i> <=10, -19<= <i>l</i> <=19
Reflections collected	16614
Independent reflections	5872 [R(int) = 0.0306]
Completeness to theta = 30.57°	98.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8794 and 0.7653
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5872 / 140 / 306
Goodness-of-fit on F ²	1.044
Final R indices [I>2sigma(I)]	R ₁ = 0.0322, wR ₂ = 0.0754
R indices (all data)	R ₁ = 0.0453, wR ₂ = 0.0887
Absolute structure parameter	0.01(3)
Largest diff. peak and hole	0.474 and -0.249 e.Å ⁻³

Table A2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex (*S*)-**85**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	6912(1)	7503(1)	7630(1)	54(1)
C(1)	7250(3)	6986(4)	6274(3)	49(1)
C(2)	6483(3)	7115(4)	5255(2)	47(1)
C(3)	5398(3)	7944(4)	5036(3)	51(1)
C(4)	4680(3)	7944(5)	4071(3)	55(1)
C(5)	4988(3)	7111(5)	3236(3)	58(1)
C(6)	4150(4)	7080(7)	2182(3)	79(2)
C(7)	6061(3)	6376(6)	3409(3)	60(1)
C(8)	6849(3)	6393(5)	4412(3)	50(1)
C(9)	7986(3)	5764(6)	4585(4)	65(1)
C(10)	8744(3)	5814(6)	5518(4)	65(1)
C(11)	9983(4)	5249(9)	5635(5)	97(2)
C(12)	8358(3)	6414(5)	6379(3)	57(1)
C(13)	9122(3)	6430(7)	7463(4)	66(1)
C(14)	9138(5)	4599(8)	7956(4)	90(2)
C(15)	9166(3)	7720(15)	9193(3)	98(2)
C(16)	8949(4)	9647(7)	7674(5)	85(2)
C(17)	6434(4)	8413(8)	9844(4)	80(1)
C(18)	6154(7)	8920(13)	10824(5)	133(3)
C(19)	4294(3)	6550(6)	6856(3)	55(1)
C(20)	3103(3)	6106(7)	6401(4)	77(1)
Cl(1)	7535(1)	3773(3)	1085(1)	99(1)
O(1)	6380(7)	3690(30)	1058(15)	188(12)
O(2)	7740(12)	3940(30)	161(8)	138(6)
O(3)	8090(9)	2330(30)	1647(18)	180(9)
O(4)	8070(13)	5030(40)	1790(19)	266(13)
O(1A)	6371(8)	3980(30)	942(19)	155(11)
O(2A)	7791(15)	2670(40)	385(19)	211(12)

O(3A)	8056(16)	3320(40)	2080(11)	171(11)
O(4A)	8052(13)	5459(19)	1132(18)	179(11)
N(1)	8656(3)	7857(6)	8046(3)	68(1)
N(2)	6647(3)	8057(5)	9108(3)	72(1)
N(3)	5229(3)	6909(4)	7157(2)	55(1)

Table A3 Crystallographic Data for Complex (*R, R*)-**90**

Empirical formula	$\text{C}_{32}\text{H}_{32}\text{Cl}_2\text{O}_4\text{P}_2\text{Pd} \cdot \text{CH}_2\text{Cl}_2$	
Formula weight	804.74	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2	
Unit cell dimensions	$a = 16.0285(6)$ Å	$\alpha = 90^\circ$.
	$b = 14.8409(6)$ Å	$\beta = 115.707(2)^\circ$.
	$c = 16.6533(6)$ Å	$\gamma = 90^\circ$.
Volume	$3569.4(2)$ Å ³	
Z	4	
Density (calculated)	1.498 Mg/m ³	
Absorption coefficient	0.944 mm^{-1}	
F(000)	1632	
Crystal size	$0.25 \times 0.25 \times 0.15 \text{ mm}^3$	
Theta range for data collection	1.97 to 30.55° .	
Index ranges	$-22 \leq h \leq 22$, $-21 \leq k \leq 21$, $-$	
	$23 \leq l \leq 23$	
Reflections collected	54211	
Independent reflections	10910 [$R(\text{int}) = 0.0270$]	
Completeness to $\theta = 30.55^\circ$	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8714 and 0.7982	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10910 / 1 / 401	
Goodness-of-fit on F^2	1.046	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0281$, $wR2 = 0.0742$	
R indices (all data)	$R1 = 0.0309$, $wR2 = 0.0763$	
Absolute structure parameter	$-0.018(13)$	
Largest diff. peak and hole	1.454 and -1.077 e.Å^{-3}	

Table A4 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (*R, R*)-**90**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	5000	543(1)	10000	22(1)
Pd(2)	5000	2707(1)	5000	21(1)
Cl(1)	4005(1)	-533(1)	10158(1)	37(1)
Cl(2)	3885(1)	1633(1)	4929(1)	32(1)
Cl(3)	5087(1)	8929(1)	4165(1)	108(1)
Cl(4)	9069(1)	1942(1)	9259(1)	108(1)
O(1)	6108(1)	3981(1)	10490(1)	35(1)
O(2)	5973(1)	3696(1)	9106(1)	31(1)
O(3)	6120(1)	6158(1)	5432(1)	36(1)
O(4)	5821(1)	5880(1)	3999(1)	30(1)
P(1)	5870(1)	1626(1)	9819(1)	22(1)
P(2)	5932(1)	3796(1)	4934(1)	21(1)
C(1)	6970(1)	1799(1)	10783(1)	22(1)
C(2)	7142(2)	1327(2)	11565(2)	30(1)
C(3)	7952(2)	1490(2)	12334(2)	39(1)
C(4)	8586(2)	2112(2)	12329(2)	38(1)
C(5)	8425(2)	2583(2)	11551(2)	36(1)
C(6)	7620(2)	2421(2)	10775(2)	29(1)
C(7)	6082(2)	1496(2)	8848(1)	30(1)
C(8)	6892(2)	1095(2)	8923(2)	47(1)
C(9)	7015(3)	896(3)	8160(2)	67(1)
C(10)	6328(3)	1095(3)	7335(2)	64(1)
C(11)	5527(3)	1484(3)	7251(2)	64(1)
C(12)	5378(2)	1679(2)	8003(2)	44(1)
C(13)	5227(1)	2701(1)	9680(1)	24(1)
C(14)	5821(2)	3538(2)	9819(2)	26(1)
C(15)	6499(2)	4517(2)	9140(2)	43(1)
C(16)	5892(2)	5328(2)	8921(2)	46(1)
C(17)	6927(2)	3996(2)	5987(1)	28(1)

C(18)	6954(2)	3587(2)	6759(2)	35(1)
C(19)	7712(2)	3731(2)	7579(2)	53(1)
C(20)	8434(2)	4261(3)	7631(2)	62(1)
C(21)	8412(2)	4672(3)	6877(3)	61(1)
C(22)	7652(2)	4544(2)	6049(2)	42(1)
C(23)	6350(2)	3692(2)	4090(1)	24(1)
C(24)	7213(2)	3299(2)	4310(2)	38(1)
C(25)	7543(2)	3206(2)	3670(2)	47(1)
C(26)	7024(2)	3516(2)	2807(2)	35(1)
C(27)	6165(2)	3896(2)	2583(2)	31(1)
C(28)	5819(2)	3974(2)	3213(1)	29(1)
C(29)	5231(1)	4850(1)	4684(1)	20(1)
C(30)	5779(1)	5709(2)	4766(1)	24(1)
C(31)	6360(2)	6662(2)	3984(2)	40(1)
C(32)	6361(3)	6670(3)	3086(2)	70(1)
C(33)	5000	9530(4)	5000	147(5)
C(34)	10000	2452(4)	10000	193(7)

Table A5 Crystallographic Data for Complex **91b**

Empirical formula	C ₃₄ H ₃₃ CINPPd	
Formula weight	628.43	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.9100(2) Å	α = 90°.
	b = 15.8210(3) Å	β = 90°.
	c = 16.7419(3) Å	γ = 90°.
Volume	2889.77(9) Å ³	
Z	4	
Density (calculated)	1.444 Mg/m ³	
Absorption coefficient	0.814 mm ⁻¹	
F(000)	1288	
Crystal size	0.30 x 0.30 x 0.24 mm ³	
Theta range for data collection	1.77 to 33.91°.	
Index ranges	-14<=h<=17, -24<=k<=24, -	
	26<=l<=26	
Reflections collected	51618	
Independent reflections	11681 [R(int) = 0.0411]	
Completeness to theta = 33.91°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8286 and 0.7923	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	11681 / 0 / 346	
Goodness-of-fit on F ²	1.134	
Final R indices [I>2sigma(I)]	R ₁ = 0.0291, wR ₂ = 0.0655	
R indices (all data)	R ₁ = 0.0395, wR ₂ = 0.0833	
Absolute structure parameter	-0.020(16)	
Largest diff. peak and hole	0.527 and -0.613 e.Å ⁻³	

Table A6 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex **91b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	4724(2)	9264(1)	1705(1)	20(1)
C(2)	4604(2)	10046(1)	2113(1)	22(1)
C(3)	3648(2)	10202(1)	2622(1)	24(1)
C(4)	2731(2)	9595(1)	2756(1)	22(1)
C(5)	1714(2)	9757(2)	3261(1)	28(1)
C(6)	824(2)	9171(2)	3374(1)	33(1)
C(7)	901(3)	8386(2)	2986(1)	32(1)
C(8)	1861(2)	8206(2)	2487(1)	28(1)
C(9)	2812(2)	8803(1)	2350(1)	21(1)
C(10)	3828(2)	8659(1)	1829(1)	21(1)
C(11)	3978(2)	7825(1)	1408(1)	24(1)
C(12)	4718(3)	7222(2)	1930(2)	36(1)
C(13)	3655(2)	8384(2)	74(1)	33(1)
C(14)	5066(3)	7229(2)	241(2)	38(1)
C(15)	7514(2)	10191(1)	2199(1)	22(1)
C(16)	7696(2)	9614(1)	2771(1)	23(1)
C(17)	7797(2)	8689(1)	2726(1)	22(1)
C(18)	7617(3)	8223(2)	3429(1)	32(1)
C(19)	7782(3)	7357(2)	3445(2)	36(1)
C(20)	8157(3)	6935(2)	2769(2)	34(1)
C(21)	8335(3)	7381(2)	2070(2)	33(1)
C(22)	8155(2)	8247(2)	2044(1)	27(1)
C(23)	8764(2)	10041(1)	721(1)	22(1)
C(24)	9823(2)	9946(2)	1176(1)	29(1)
C(25)	10969(2)	9976(2)	817(2)	36(1)
C(26)	11072(3)	10100(2)	2(2)	36(1)
C(27)	10026(3)	10195(2)	-459(2)	31(1)
C(28)	8887(2)	10166(1)	-108(1)	26(1)

C(29)	6607(2)	11046(1)	817(1)	20(1)
C(30)	7208(2)	11805(1)	972(1)	26(1)
C(31)	6686(2)	12564(1)	740(2)	31(1)
C(32)	5570(3)	12575(2)	352(2)	33(1)
C(33)	4973(2)	11821(2)	185(2)	31(1)
C(34)	5486(2)	11063(2)	422(1)	27(1)
Cl(1)	6858(1)	8713(1)	-450(1)	36(1)
N(1)	4587(2)	8013(1)	618(1)	24(1)
P(1)	7221(1)	10031(1)	1145(1)	19(1)
Pd(1)	5907(1)	8980(1)	821(1)	19(1)

Table A7 Crystallographic Data for Complexes **93a,b**

Empirical formula	$C_{46}H_{44}ClNO_4P_2Pd$	
Formula weight	878.61	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	$a = 9.8084(4)$ Å	$\alpha = 79.220(2)^\circ$.
	$b = 13.7477(4)$ Å	$\beta = 88.686(2)^\circ$.
	$c = 15.7166(5)$ Å	$\gamma = 89.995(2)^\circ$.
Volume	$2081.31(12)$ Å ³	
Z	2	
Density (calculated)	1.402 Mg/m ³	
Absorption coefficient	0.631 mm ⁻¹	
F(000)	904	
Crystal size	0.10 x 0.10 x 0.10 mm ³	
Theta range for data collection	2.08 to 28.38°.	
Index ranges	-13 ≤ h ≤ 13, -18 ≤ k ≤ 18, -	
	20 ≤ l ≤ 20	
Reflections collected	51004	
Independent reflections	19402 [R(int) = 0.0259]	
Completeness to theta = 28.38°	99.5 %	
Absorption correction	None	
Max. and min. transmission	0.9396 and 0.9396	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	19402 / 3 / 997	
Goodness-of-fit on F ²	1.020	
Final R indices [I > 2σ(I)]	R ₁ = 0.0353, wR ₂ = 0.0827	
R indices (all data)	R ₁ = 0.0457, wR ₂ = 0.0878	
Absolute structure parameter	-0.022(13)	
Largest diff. peak and hole	0.749 and -0.305 e.Å ⁻³	

Table A8 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Complexes **93a,b**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	9037(1)	2237(1)	1140(1)	40(1)
Pd(2)	8190(1)	7374(1)	6013(1)	41(1)
Cl(1)	2576(2)	9390(1)	3078(1)	103(1)
Cl(2)	4216(2)	4474(1)	8056(1)	120(1)
N(1)	10521(4)	2725(2)	126(2)	63(1)
N(2)	7264(4)	8000(2)	4819(2)	59(1)
O(1)	3250(20)	9301(10)	3648(9)	481(15)
O(2)	1260(8)	9309(7)	3133(7)	232(4)
O(3)	2668(11)	10292(5)	2599(8)	271(6)
O(4)	2824(10)	8611(6)	2603(7)	229(4)
O(5)	3987(9)	3610(5)	7727(6)	225(4)
O(6)	5586(7)	4539(6)	8058(5)	200(3)
O(7)	4008(12)	5279(7)	7439(9)	349(9)
O(8)	3479(14)	4443(9)	8683(7)	353(9)
P(1)	8401(1)	704(1)	796(1)	37(1)
P(2)	7536(1)	1832(1)	2250(1)	38(1)
P(3)	8820(1)	5790(1)	5753(1)	45(1)
P(4)	9382(1)	6953(1)	7221(1)	42(1)
C(1)	9639(3)	3557(2)	1477(2)	45(1)
C(2)	9516(4)	3886(3)	2267(2)	51(1)
C(3)	10056(4)	4761(3)	2389(2)	53(1)
C(4)	10799(3)	5372(2)	1722(2)	49(1)
C(5)	11411(4)	6273(3)	1838(3)	64(1)
C(6)	12166(5)	6827(3)	1197(3)	79(1)
C(7)	12337(5)	6519(3)	402(4)	83(1)
C(8)	11757(5)	5669(3)	254(3)	66(1)
C(9)	10949(3)	5062(2)	909(2)	49(1)
C(10)	10334(4)	4162(2)	802(2)	50(1)
C(11)	10350(5)	3841(3)	-64(2)	68(1)

C(12)	9080(7)	4147(4)	-534(3)	97(2)
C(13)	11901(5)	2470(3)	482(4)	87(2)
C(14)	10441(7)	2345(3)	-690(3)	95(2)
C(15)	6817(3)	598(2)	2233(2)	41(1)
C(16)	7875(3)	-45(2)	1866(2)	36(1)
C(17)	6943(4)	730(3)	110(2)	51(1)
C(18)	6327(5)	1632(4)	-193(3)	76(1)
C(19)	5183(6)	1652(6)	-743(4)	104(2)
C(20)	4734(6)	804(7)	-978(4)	110(2)
C(21)	5343(5)	-77(6)	-684(3)	94(2)
C(22)	6439(4)	-129(4)	-137(2)	64(1)
C(23)	9704(3)	17(2)	324(2)	40(1)
C(24)	9625(4)	-173(3)	-517(2)	57(1)
C(25)	10725(5)	-591(3)	-879(3)	77(1)
C(26)	11888(5)	-817(3)	-420(4)	79(1)
C(27)	11991(5)	-606(3)	410(4)	76(1)
C(28)	10894(4)	-202(3)	778(3)	55(1)
C(29)	7412(3)	-1104(2)	1900(2)	38(1)
C(30)	8365(4)	-1857(3)	1971(2)	50(1)
C(31)	7959(5)	-2835(3)	2046(3)	61(1)
C(32)	6620(5)	-3079(3)	2061(2)	62(1)
C(33)	5657(4)	-2345(3)	1985(2)	62(1)
C(34)	6040(4)	-1366(3)	1898(2)	52(1)
C(35)	6039(3)	2610(2)	2253(2)	47(1)
C(36)	6055(5)	3570(3)	1784(3)	68(1)
C(37)	4875(6)	4149(3)	1785(4)	90(2)
C(38)	3744(6)	3776(5)	2229(4)	97(2)
C(39)	3709(5)	2822(4)	2693(4)	85(1)
C(40)	4847(4)	2251(3)	2698(3)	65(1)
C(41)	8296(3)	1689(2)	3316(2)	43(1)
C(42)	7592(4)	1899(3)	4031(2)	57(1)
C(43)	8232(6)	1771(4)	4822(3)	81(1)
C(44)	9513(7)	1432(4)	4909(3)	89(2)
C(45)	10226(5)	1207(4)	4201(3)	85(1)
C(46)	9607(4)	1349(3)	3397(2)	61(1)
C(47)	7371(4)	8642(2)	6339(2)	46(1)

C(48)	7632(4)	9108(3)	7057(2)	51(1)
C(49)	7002(4)	9951(3)	7157(3)	59(1)
C(50)	6027(4)	10416(3)	6562(3)	59(1)
C(51)	5384(5)	11317(3)	6644(3)	71(1)
C(52)	4473(5)	11742(3)	6058(4)	88(2)
C(53)	4149(5)	11303(4)	5357(4)	88(2)
C(54)	4748(4)	10425(3)	5255(3)	71(1)
C(55)	5728(4)	9968(3)	5835(2)	55(1)
C(56)	6409(4)	9071(2)	5755(2)	51(1)
C(57)	6019(4)	8512(3)	5062(2)	62(1)
C(58)	4857(5)	7803(4)	5395(4)	87(1)
C(59)	8265(6)	8752(3)	4353(3)	77(1)
C(60)	6934(7)	7330(3)	4209(3)	88(2)
C(61)	10078(4)	5702(3)	7268(2)	58(1)
C(62)	9122(4)	5079(2)	6869(2)	53(1)
C(63)	7509(3)	5103(2)	5315(2)	46(1)
C(64)	6289(4)	4894(3)	5777(3)	60(1)
C(65)	5260(4)	4405(4)	5447(4)	81(1)
C(66)	5432(5)	4142(3)	4649(4)	83(1)
C(67)	6594(5)	4369(3)	4178(3)	74(1)
C(68)	7631(4)	4851(3)	4502(3)	60(1)
C(69)	10340(4)	5693(3)	5095(2)	55(1)
C(70)	10780(4)	4785(4)	4911(3)	68(1)
C(71)	11897(5)	4757(5)	4383(3)	88(2)
C(72)	12609(5)	5585(6)	4033(4)	100(2)
C(73)	12222(5)	6485(5)	4226(3)	96(2)
C(74)	11063(4)	6537(4)	4767(3)	72(1)
C(75)	9556(4)	4000(2)	6942(2)	51(1)
C(76)	8545(6)	3285(3)	7062(3)	83(1)
C(77)	8875(8)	2311(4)	7140(5)	113(3)
C(78)	10171(9)	2005(3)	7142(3)	101(2)
C(79)	11178(7)	2700(4)	7041(3)	97(2)
C(80)	10871(5)	3700(3)	6936(3)	73(1)
C(81)	10912(4)	7695(3)	7245(2)	56(1)
C(82)	11021(5)	8646(3)	6768(3)	70(1)
C(83)	12164(7)	9215(4)	6814(4)	97(2)

C(84)	13221(7)	8842(6)	7295(5)	116(3)
C(85)	13186(5)	7908(6)	7752(4)	99(2)
C(86)	12009(4)	7322(4)	7735(3)	73(1)
C(87)	8458(4)	6911(2)	8246(2)	46(1)
C(88)	9076(5)	7130(3)	8974(2)	64(1)
C(89)	8338(6)	7058(4)	9744(3)	87(2)
C(90)	7017(6)	6735(5)	9791(3)	95(2)
C(91)	6398(5)	6473(5)	9081(3)	91(2)
C(92)	7108(4)	6583(3)	8305(3)	67(1)

Table A9 Crystallographic Data for Complex (*R*)-**94**

Empirical formula	$\text{C}_{33}\text{H}_{30}\text{Cl}_4\text{P}_2\text{Pd}$	
Formula weight	736.71	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	$a = 8.7544(4)$ Å	$\alpha = 99.976(2)^\circ$.
	$b = 8.7570(4)$ Å	$\beta = 104.330(2)^\circ$.
	$c = 11.2458(5)$ Å	$\gamma = 100.603(2)^\circ$.
Volume	$799.08(6)$ Å ³	
Z	1	
Density (calculated)	1.531 Mg/m ³	
Absorption coefficient	1.037 mm ⁻¹	
F(000)	372	
Crystal size	$0.20 \times 0.15 \times 0.10$ mm ³	
Theta range for data collection	1.92 to 30.55° .	
Index ranges	$-12 \leq h \leq 12$, $-12 \leq k \leq 12$, $-15 \leq l \leq 16$	
Reflections collected	19537	
Independent reflections	9375 [$R(\text{int}) = 0.0283$]	
Completeness to $\theta = 30.55^\circ$	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9034 and 0.8194	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9375 / 3 / 361	
Goodness-of-fit on F^2	1.102	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0311$, $wR_2 = 0.0819$	
R indices (all data)	$R_1 = 0.0319$, $wR_2 = 0.0830$	
Absolute structure parameter	0.023(18)	
Largest diff. peak and hole	0.961 and -1.001 e.Å ⁻³	

Table A10 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex (*R*)-**94**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	672(1)	4583(1)	864(1)	18(1)
Cl(1)	-784(1)	5259(1)	-966(1)	31(1)
Cl(2)	-1639(1)	4044(1)	1578(1)	32(1)
P(1)	3114(1)	5255(1)	538(1)	18(1)
P(2)	1966(1)	3736(1)	2506(1)	18(1)
C(1)	3815(4)	7297(3)	412(3)	22(1)
C(2)	2807(5)	7969(5)	-400(4)	34(1)
C(3)	3361(5)	9499(5)	-543(4)	40(1)
C(4)	4915(5)	10374(4)	111(4)	36(1)
C(5)	5910(7)	9720(7)	898(6)	50(1)
C(6)	5373(5)	8187(5)	1075(4)	43(1)
C(7)	3344(4)	4007(3)	-842(3)	20(1)
C(8)	1987(4)	2964(4)	-1746(3)	26(1)
C(9)	2191(5)	2021(4)	-2807(3)	31(1)
C(10)	3717(5)	2122(4)	-2969(3)	32(1)
C(11)	5065(4)	3159(4)	-2080(3)	29(1)
C(12)	4888(4)	4116(4)	-1024(3)	25(1)
C(13)	4654(4)	4999(4)	1882(3)	22(1)
C(14)	3972(4)	3495(4)	2292(3)	21(1)
C(15)	5104(4)	3122(4)	3410(3)	27(1)
C(16)	4908(5)	1552(5)	3548(4)	36(1)
C(17)	5930(6)	1182(6)	4579(5)	48(1)
C(18)	7132(6)	2357(7)	5457(4)	48(1)
C(19)	7355(6)	3914(6)	5333(4)	47(1)
C(20)	6344(5)	4300(5)	4310(4)	38(1)
C(21)	934(4)	1814(4)	2646(3)	22(1)
C(22)	826(4)	465(4)	1717(3)	30(1)
C(23)	51(5)	-1047(4)	1778(4)	39(1)
C(24)	-604(5)	-1220(4)	2773(4)	39(1)

C(25)	-545(5)	108(5)	3662(4)	37(1)
C(26)	224(4)	1633(4)	3604(3)	28(1)
C(27)	2423(4)	5186(4)	3977(3)	21(1)
C(28)	3047(5)	4863(4)	5140(3)	31(1)
C(29)	3410(6)	6048(5)	6245(4)	41(1)
C(30)	3171(6)	7555(5)	6179(4)	47(1)
C(31)	2592(6)	7895(5)	5020(4)	49(1)
C(32)	2199(5)	6716(4)	3919(3)	34(1)
C(33)	7885(9)	8437(11)	7719(10)	121(4)
CI(3)	8089(3)	10456(3)	8507(2)	105(1)
CI(4)	8849(4)	8310(3)	6529(3)	133(1)

Table A11 Crystallographic Data for Complex **99a**

Empirical formula	$\text{C}_{39}\text{H}_{44}\text{Cl}_3\text{NO}_4\text{P}_2\text{Pd}$	
Formula weight	865.44	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	$a = 9.3975(5)$ Å	$\alpha = 90^\circ$.
	$b = 9.8036(6)$ Å	$\beta = 92.841(3)^\circ$.
	$c = 20.7827(11)$ Å	$\gamma = 90^\circ$.
Volume	$1912.34(19)$ Å ³	
Z	2	
Density (calculated)	1.503 Mg/m ³	
Absorption coefficient	0.820 mm ⁻¹	
F(000)	888	
Crystal size	0.24 x 0.22 x 0.10 mm ³	
Theta range for data collection	1.96 to 33.39°.	
Index ranges	-14 ≤ h ≤ 14, -15 ≤ k ≤ 14, -	
	32 ≤ l ≤ 29	
Reflections collected	37064	
Independent reflections	13784 [R(int) = 0.0343]	
Completeness to theta = 33.39°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9225 and 0.8275	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	13784 / 13 / 456	
Goodness-of-fit on F ²	1.071	
Final R indices [I > 2σ(I)]	R ₁ = 0.0379, wR ₂ = 0.0928	
R indices (all data)	R ₁ = 0.0485, wR ₂ = 0.1037	
Absolute structure parameter	0.003(17)	
Largest diff. peak and hole	1.153 and -0.951 e.Å ⁻³	

Table A12 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex **99a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	6216(1)	715(1)	7419(1)	19(1)
C(1)	5410(3)	1465(3)	8251(1)	21(1)
C(2)	5687(3)	1066(3)	8903(1)	23(1)
C(3)	5004(3)	1657(3)	9399(1)	25(1)
C(4)	3992(3)	2712(3)	9280(1)	22(1)
C(5)	3258(3)	3335(4)	9784(1)	29(1)
C(6)	2300(3)	4346(3)	9662(2)	31(1)
C(7)	2002(3)	4794(3)	9023(1)	28(1)
C(8)	2682(3)	4219(3)	8520(1)	24(1)
C(9)	3694(3)	3159(3)	8629(1)	20(1)
C(10)	4440(3)	2514(3)	8129(1)	20(1)
C(11)	4243(3)	2997(3)	7441(1)	23(1)
C(12)	5350(3)	4098(3)	7309(1)	28(1)
C(13)	4364(3)	2214(4)	6329(1)	29(1)
C(14)	3105(3)	892(4)	7084(1)	28(1)
C(15)	6065(3)	-502(3)	5790(1)	25(1)
C(16)	4852(3)	-1282(3)	5908(2)	30(1)
C(17)	3773(4)	-1420(4)	5429(2)	38(1)
C(18)	3893(4)	-765(4)	4835(2)	41(1)
C(19)	5098(4)	-40(4)	4717(2)	36(1)
C(20)	6182(3)	107(3)	5187(1)	29(1)
C(21)	8578(3)	1071(3)	6157(1)	26(1)
C(22)	8601(3)	2446(4)	6337(2)	32(1)
C(23)	9596(4)	3325(4)	6102(2)	44(1)
C(24)	10590(4)	2869(5)	5692(2)	48(1)
C(25)	10588(4)	1505(5)	5499(2)	47(1)
C(26)	9593(3)	633(5)	5734(1)	39(1)
C(27)	7469(4)	-2877(4)	6794(2)	37(1)
C(28)	8349(3)	-1576(3)	6720(1)	27(1)

C(29)	9185(3)	-1127(3)	7337(1)	27(1)
C(30)	9165(3)	392(3)	8537(1)	27(1)
C(31)	9641(4)	1665(4)	8520(2)	35(1)
C(32)	9318(5)	2707(5)	8034(2)	61(1)
C(33)	7408(3)	-1954(3)	8360(1)	23(1)
C(34)	5974(3)	-2283(3)	8368(1)	26(1)
C(35)	5550(3)	-3476(3)	8666(2)	30(1)
C(36)	6557(3)	-4357(5)	8948(1)	33(1)
C(37)	7994(4)	-4022(4)	8944(2)	37(1)
C(38)	8423(3)	-2822(3)	8656(2)	31(1)
C(39)	2633(5)	8960(6)	9376(3)	69(1)
Cl(1)	2046(1)	6489(1)	6784(1)	48(1)
Cl(2)	1391(1)	8198(1)	9865(1)	56(1)
Cl(3)	2369(1)	8497(1)	8560(1)	56(1)
N(1)	4377(2)	1778(3)	7015(1)	21(1)
O(1)	2687(5)	5523(5)	6418(2)	90(1)
O(2)	1059(3)	5886(4)	7198(2)	58(1)
O(3)	1426(6)	7492(9)	6420(3)	204(5)
O(4)	3210(8)	7075(7)	7181(3)	150(3)
P(1)	7259(1)	-79(1)	6474(1)	22(1)
P(2)	7992(1)	-437(1)	7939(1)	21(1)

Table A13 Crystallographic Data for Complex **99b,d**

Empirical formula	C ₃₈ H ₄₂ Cl N O ₄ P ₂ Pd
Formula weight	780.52
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)
Unit cell dimensions	a = 19.480(2) Å α = 90°. b = 9.6937(11) Å β = 109.602(7)°. c = 20.358(2) Å γ = 90°.
Volume	3621.5(7) Å ³
Z	4
Density (calculated)	1.432 Mg/m ³
Absorption coefficient	0.715 mm ⁻¹
F(000)	1608
Crystal size	0.32 x 0.24 x 0.02 mm ³
Theta range for data collection	1.06 to 25.00°.
Index ranges	-23 ≤ h ≤ 23, -10 ≤ k ≤ 11, - 24 ≤ l ≤ 24
Reflections collected	52186
Independent reflections	11928 [R(int) = 0.1341]
Completeness to theta = 25.00°	99.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9858 and 0.8036
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	11928 / 2 / 857
Goodness-of-fit on F ²	1.056
Final R indices [I > 2σ(I)]	R1 = 0.0686, wR2 = 0.1644
R indices (all data)	R1 = 0.0990, wR2 = 0.2095
Absolute structure parameter	-0.02(4)
Largest diff. peak and hole	0.775 and -2.585 e.Å ⁻³

Table A14 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex **99b,d**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	2278(1)	9696(1)	2525(1)	25(1)
Pd(2)	6998(1)	791(1)	2493(1)	28(1)
C(1)	2846(5)	9456(12)	4177(5)	29(3)
C(2)	3297(5)	9843(14)	4820(5)	33(3)
C(3)	3860(6)	10810(14)	4898(5)	35(2)
C(4)	4347(6)	11230(14)	5564(5)	38(3)
C(5)	4878(6)	12137(15)	5635(6)	45(3)
C(6)	4960(6)	12727(14)	5038(6)	39(3)
C(7)	4526(5)	12357(13)	4381(6)	36(3)
C(8)	3952(5)	11404(12)	4296(5)	29(2)
C(9)	3466(5)	10974(13)	3626(5)	30(2)
C(10)	2936(5)	9998(13)	3566(4)	31(3)
C(11)	3564(6)	11538(13)	2969(5)	34(3)
C(12)	4094(5)	10590(16)	2755(5)	43(3)
C(13)	2889(6)	11847(13)	1712(5)	35(3)
C(14)	2399(6)	12692(15)	2576(5)	40(3)
C(15)	945(5)	11029(12)	1058(5)	31(3)
C(16)	522(6)	11530(15)	1450(6)	44(3)
C(17)	166(7)	12709(15)	1296(7)	51(3)
C(18)	219(8)	13535(17)	728(8)	61(4)
C(19)	630(7)	13064(16)	356(7)	56(4)
C(20)	990(6)	11794(15)	504(6)	40(3)
C(21)	1794(6)	9031(13)	651(5)	36(3)
C(22)	2443(7)	8540(14)	691(6)	42(3)
C(23)	3083(7)	8230(15)	1304(6)	48(3)
C(24)	825(6)	8116(14)	1379(6)	37(3)
C(25)	1173(6)	6977(14)	1901(6)	41(3)
C(26)	1703(7)	6066(13)	1684(6)	43(3)
C(27)	912(5)	8556(12)	3021(5)	27(2)

C(28)	1006(6)	9791(16)	3393(6)	41(3)
C(29)	449(7)	10295(15)	3606(6)	46(3)
C(30)	-210(7)	9590(18)	3432(7)	53(3)
C(31)	-301(7)	8393(17)	3059(7)	51(3)
C(32)	258(6)	7860(14)	2865(7)	44(3)
C(33)	2148(5)	6583(13)	3331(5)	31(3)
C(34)	1797(6)	5732(15)	3679(6)	42(3)
C(35)	2185(6)	4735(16)	4141(5)	45(3)
C(36)	2923(6)	4539(15)	4254(5)	42(3)
C(37)	3266(6)	5356(13)	3903(6)	41(3)
C(38)	2884(6)	6355(13)	3449(6)	34(3)
C(39)	7835(5)	1476(12)	3376(5)	27(2)
C(40)	7968(6)	1109(12)	4067(5)	36(3)
C(41)	8583(6)	1593(13)	4569(5)	35(3)
C(42)	9114(6)	2384(13)	4403(6)	35(3)
C(43)	9761(6)	2794(14)	4933(6)	40(3)
C(44)	10259(6)	3612(15)	4769(6)	44(3)
C(45)	10106(6)	4003(14)	4059(6)	44(3)
C(46)	9496(6)	3598(13)	3548(5)	33(3)
C(47)	8981(5)	2744(12)	3695(5)	29(2)
C(48)	8337(5)	2273(12)	3185(5)	28(2)
C(49)	8170(6)	2659(14)	2431(5)	36(3)
C(50)	8545(6)	1657(15)	2093(6)	44(3)
C(51)	7136(7)	2762(17)	1317(6)	56(4)
C(52)	7047(6)	3833(15)	2335(7)	48(3)
C(53)	7377(5)	-2102(12)	3557(5)	25(2)
C(54)	7453(6)	-2630(14)	4207(5)	39(3)
C(55)	7979(6)	-3522(15)	4529(6)	45(3)
C(56)	8448(6)	-4040(14)	4213(6)	42(3)
C(57)	8389(7)	-3565(15)	3563(7)	48(3)
C(58)	7873(6)	-2576(14)	3223(6)	36(3)
C(59)	6217(5)	-488(14)	3680(5)	35(3)
C(60)	6019(6)	747(17)	3849(6)	44(3)
C(61)	6108(8)	2132(18)	3603(8)	61(4)
C(62)	6002(6)	-2013(13)	2451(5)	35(3)
C(63)	6146(6)	-2113(13)	1756(5)	36(3)

C(64)	5607(7)	-3066(15)	1228(6)	48(3)
C(65)	5272(6)	374(13)	1083(5)	36(3)
C(66)	4755(6)	-264(16)	525(5)	41(3)
C(67)	4059(6)	280(15)	254(6)	45(3)
C(68)	3888(6)	1496(16)	530(6)	45(3)
C(69)	4398(6)	2127(14)	1084(6)	43(3)
C(70)	5091(6)	1545(13)	1367(5)	36(3)
C(71)	6570(6)	-440(14)	763(5)	37(3)
C(72)	7233(6)	-1044(14)	891(6)	42(3)
C(73)	7586(8)	-1019(16)	403(8)	62(4)
C(74)	7233(9)	-360(20)	-238(7)	72(5)
C(75)	6550(9)	217(17)	-378(7)	63(4)
C(76)	6233(7)	198(14)	135(6)	45(3)
Cl(1)	8760(2)	5867(4)	1471(2)	55(1)
Cl(2)	5581(2)	298(3)	7515(1)	45(1)
N(1)	2824(4)	11550(9)	2418(4)	21(2)
N(2)	7353(5)	2590(11)	2094(5)	36(2)
O(1)	8398(7)	4962(17)	935(6)	112(6)
O(2)	9338(6)	5116(11)	2002(6)	71(3)
O(3)	9075(6)	6946(14)	1214(6)	85(4)
O(4)	8278(6)	6373(13)	1810(5)	78(3)
O(5)	5433(6)	-449(13)	6889(5)	74(3)
O(6)	5525(6)	1757(11)	7360(5)	75(3)
O(7)	5099(8)	-21(18)	7875(8)	128(6)
O(8)	6307(6)	-12(13)	7966(5)	79(4)
P(1)	1493(1)	9463(3)	1369(1)	29(1)
P(2)	1652(1)	7903(3)	2732(1)	26(1)
P(3)	6205(1)	-290(4)	1480(1)	30(1)
P(4)	6667(1)	-912(3)	3070(1)	28(1)

Table A15 Crystallographic Data for Complex **104a**

Empirical formula	$\text{C}_{38}\text{H}_{42}\text{ClNO}_4\text{P}_2\text{Pd}$	
Formula weight	780.52	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	$a = 13.1140(5)$ Å	$\alpha = 90^\circ$.
	$b = 14.5210(5)$ Å	$\beta = 90^\circ$.
	$c = 19.8323(7)$ Å	$\gamma = 90^\circ$.
Volume	$3776.6(2)$ Å ³	
Z	4	
Density (calculated)	1.373 Mg/m ³	
Absorption coefficient	0.685 mm ⁻¹	
F(000)	1608	
Crystal size	0.20 x 0.15 x 0.04 mm ³	
Theta range for data collection	2.05 to 27.50°.	
Index ranges	-17 ≤ h ≤ 17, -18 ≤ k ≤ 18, -	
	25 ≤ l ≤ 25	
Reflections collected	72744	
Independent reflections	8671 [R(int) = 0.0917]	
Completeness to theta = 27.50°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9731 and 0.8751	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8671 / 0 / 399	
Goodness-of-fit on F ²	1.075	
Final R indices [I > 2σ(I)]	R ₁ = 0.0514, wR ₂ = 0.1167	
R indices (all data)	R ₁ = 0.0884, wR ₂ = 0.1464	
Absolute structure parameter	0.01(4)	
Largest diff. peak and hole	0.638 and -0.598 e.Å ⁻³	

Table A16 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex **104a**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	7400(1)	5024(1)	467(1)	46(1)
P(1)	5935(1)	5603(1)	-80(1)	53(1)
P(2)	6347(1)	4770(1)	1341(1)	54(1)
N(1)	8503(4)	5238(4)	-309(2)	58(1)
C(1)	8692(4)	4592(4)	962(3)	47(1)
C(2)	8872(5)	4481(5)	1660(3)	59(2)
C(3)	9807(5)	4303(5)	1912(3)	65(2)
C(4)	10655(4)	4179(4)	1489(3)	54(2)
C(5)	11648(6)	3983(5)	1742(4)	74(2)
C(6)	12440(6)	3837(5)	1312(4)	82(2)
C(7)	12298(5)	3875(5)	610(5)	83(2)
C(8)	11368(5)	4083(5)	363(4)	63(2)
C(9)	10523(4)	4243(4)	783(3)	49(1)
C(10)	9507(4)	4461(4)	544(3)	45(1)
C(11)	9317(5)	4511(5)	-209(3)	59(2)
C(12)	9001(6)	3589(5)	-466(4)	84(2)
C(13)	8141(6)	5224(6)	-1029(3)	84(3)
C(14)	8944(5)	6163(5)	-188(4)	74(2)
C(15)	5307(5)	4746(4)	-621(3)	56(2)
C(16)	5711(5)	3869(4)	-628(3)	64(2)
C(17)	5286(7)	3182(5)	-995(4)	85(2)
C(18)	4442(7)	3373(6)	-1404(5)	101(3)
C(19)	4044(7)	4245(6)	-1406(5)	99(3)
C(20)	4466(5)	4941(6)	-1015(4)	83(2)
C(21)	6015(5)	6654(4)	-570(4)	63(2)
C(22)	5982(9)	6662(5)	-1275(5)	111(3)
C(23)	6092(11)	7499(8)	-1606(6)	153(6)
C(24)	6279(10)	8265(7)	-1296(8)	138(5)

C(25)	6355(6)	8283(5)	-613(7)	99(3)
C(26)	6255(5)	7458(4)	-244(4)	72(2)
C(27)	5035(5)	5874(5)	606(4)	71(2)
C(28)	3954(6)	6162(6)	407(5)	105(3)
C(29)	5024(4)	4998(6)	1068(3)	72(2)
C(30)	6494(6)	5542(4)	2045(3)	67(2)
C(31)	7146(7)	6203(5)	2060(4)	86(2)
C(32)	7346(11)	6866(6)	2619(5)	130(4)
C(33)	6289(5)	3613(4)	1675(3)	58(2)
C(34)	5759(8)	3403(6)	2246(5)	109(3)
C(35)	5674(10)	2518(7)	2469(6)	140(5)
C(36)	6119(8)	1791(6)	2126(5)	105(3)
C(37)	6594(7)	1986(5)	1525(5)	86(2)
C(38)	6706(6)	2878(4)	1316(4)	70(2)
CI(1)	1576(2)	5990(2)	8542(1)	99
O(1)	918(6)	6742(5)	8633(4)	125
O(2)	1658(8)	5415(6)	9096(4)	178
O(3)	1324(11)	5577(8)	7973(7)	274
O(4)	2560(8)	6292(9)	8417(6)	256

Table A17 Crystallographic Data for Complex **104c**

Empirical formula	$\text{C}_{38}\text{H}_{42}\text{ClNO}_4\text{P}_2\text{Pd}$	
Formula weight	780.52	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	$a = 10.2187(3)$ Å	$\alpha = 90^\circ$.
	$b = 14.3113(6)$ Å	$\beta = 90^\circ$.
	$c = 25.2550(11)$ Å	$\gamma = 90^\circ$.
Volume	$3693.4(2)$ Å ³	
Z	4	
Density (calculated)	1.404 Mg/m ³	
Absorption coefficient	0.701 mm ⁻¹	
F(000)	1608	
Crystal size	0.25 x 0.10 x 0.10 mm ³	
Theta range for data collection	1.61 to 25.50°.	
Index ranges	-11 ≤ h ≤ 12, -17 ≤ k ≤ 17, -	
	30 ≤ l ≤ 30	
Reflections collected	20651	
Independent reflections	6697 [R(int) = 0.0537]	
Completeness to theta = 25.50°	98.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9332 and 0.8443	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6697 / 0 / 429	
Goodness-of-fit on F ²	1.038	
Final R indices [I > 2σ(I)]	R ₁ = 0.0567, wR ₂ = 0.1435	
R indices (all data)	R ₁ = 0.0638, wR ₂ = 0.1506	
Absolute structure parameter	0.00(5)	
Largest diff. peak and hole	1.268 and -0.509 e.Å ⁻³	

Table A18 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex **104c**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	5145(1)	9107(1)	8809(1)	37(1)
N(1)	5595(5)	7645(3)	8750(2)	40(1)
P(1)	7186(2)	9783(1)	8575(1)	39(1)
P(2)	4462(2)	10620(1)	8848(1)	52(1)
C(1)	3333(6)	8538(4)	9007(2)	39(1)
C(2)	2327(7)	8927(5)	9310(3)	49(2)
C(3)	1218(7)	8426(5)	9419(3)	50(2)
C(4)	1026(7)	7536(5)	9215(3)	49(2)
C(5)	-152(9)	7042(5)	9297(3)	66(2)
C(6)	-388(11)	6197(6)	9064(5)	94(3)
C(7)	619(11)	5789(7)	8745(4)	89(3)
C(8)	1785(9)	6226(5)	8672(4)	69(2)
C(9)	2031(7)	7120(4)	8901(3)	48(2)
C(10)	3222(6)	7634(4)	8823(2)	42(1)
C(11)	4345(7)	7233(5)	8521(3)	46(2)
C(12)	4208(10)	7417(7)	7935(3)	72(2)
C(13)	5806(8)	7264(5)	9293(3)	54(2)
C(14)	6715(8)	7363(5)	8426(3)	62(2)
C(15)	8223(7)	9285(4)	8057(3)	47(2)
C(16)	7706(9)	9248(6)	7545(3)	64(2)
C(17)	8434(13)	8822(7)	7151(3)	88(3)
C(18)	9607(12)	8424(7)	7254(4)	85(3)
C(19)	10110(11)	8456(6)	7756(4)	79(2)
C(20)	9399(8)	8875(6)	8155(3)	64(2)
C(21)	8213(8)	9984(5)	9156(3)	48(2)
C(22)	9405(8)	10461(5)	9143(3)	57(2)
C(23)	10039(10)	10685(5)	9605(4)	75(2)
C(24)	9555(11)	10430(8)	10074(4)	86(3)
C(25)	8427(13)	9937(8)	10106(3)	87(3)

C(26)	7723(10)	9723(6)	9650(3)	65(2)
C(27)	7903(8)	11596(5)	8162(3)	61(2)
C(28)	6763(7)	10970(5)	8326(3)	51(2)
C(29)	5883(8)	11387(5)	8720(4)	65(2)
C(30)	3291(9)	10950(9)	8366(4)	87(3)
C(31)	2682(10)	10453(7)	8060(4)	79(3)
C(32)	1712(11)	10773(9)	7615(4)	92(3)
C(33)	3907(8)	11114(5)	9474(4)	60(2)
C(34)	4084(11)	10686(6)	9934(4)	79(3)
C(35)	3677(14)	11079(7)	10408(5)	106(4)
C(36)	3010(14)	11896(8)	10408(5)	106(4)
C(37)	2856(15)	12361(7)	9962(5)	112(5)
C(38)	3289(11)	12006(6)	9475(5)	93(3)
Cl(1)	4382(3)	9365(1)	6660(1)	78(1)
O(1)	4779(11)	9938(6)	7087(4)	136(4)
O(2)	3813(14)	9910(6)	6287(3)	149(5)
O(3)	3330(20)	8795(10)	6834(6)	256(10)
O(4)	5263(18)	8761(10)	6490(6)	219(8)

Table A19 Crystallographic Data for Complex **105a**

Empirical formula	$\text{C}_{24}\text{H}_{26}\text{Cl}_2\text{P}_2\text{Pd}$	
Formula weight	553.69	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	$a = 8.7848(4)$ Å	$\alpha = 90^\circ$.
	$b = 12.6437(6)$ Å	$\beta = 98.203(2)^\circ$.
	$c = 11.0905(5)$ Å	$\gamma = 90^\circ$.
Volume	$1219.24(10)$ Å ³	
Z	2	
Density (calculated)	1.508 Mg/m ³	
Absorption coefficient	1.120 mm ⁻¹	
F(000)	560	
Crystal size	0.30 x 0.20 x 0.20 mm ³	
Theta range for data collection	2.46 to 30.56°.	
Index ranges	-12 ≤ h ≤ 12, -18 ≤ k ≤ 18, -	
	15 ≤ l ≤ 15	
Reflections collected	20206	
Independent reflections	7239 [R(int) = 0.0251]	
Completeness to theta = 30.56°	98.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8070 and 0.7299	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7239 / 1 / 264	
Goodness-of-fit on F ²	1.134	
Final R indices [I > 2σ(I)]	R ₁ = 0.0246, wR ₂ = 0.0664	
R indices (all data)	R ₁ = 0.0267, wR ₂ = 0.0751	
Absolute structure parameter	-0.02(2)	
Largest diff. peak and hole	0.788 and -0.940 e.Å ⁻³	

Table A20 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex **105a**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	5490(1)	5498(1)	1912(1)	19(1)
Cl(1)	5781(1)	3794(1)	2790(1)	27(1)
Cl(2)	6746(1)	5107(1)	210(1)	32(1)
P(1)	4193(1)	6016(1)	3398(1)	22(1)
P(2)	5242(1)	7158(1)	1248(1)	24(1)
C(1)	5392(4)	6029(2)	4874(3)	26(1)
C(2)	6979(4)	5951(3)	4919(3)	30(1)
C(3)	7922(5)	5950(3)	6043(4)	39(1)
C(4)	7291(5)	6015(3)	7122(4)	42(1)
C(5)	5707(5)	6086(3)	7072(3)	40(1)
C(6)	4761(5)	6100(3)	5960(3)	36(1)
C(7)	2501(4)	5241(2)	3582(3)	27(1)
C(8)	2626(4)	4367(3)	4362(4)	37(1)
C(9)	1324(5)	3751(4)	4455(5)	49(1)
C(10)	-73(5)	3988(4)	3795(4)	46(1)
C(11)	-198(4)	4830(4)	3004(4)	43(1)
C(12)	1079(3)	5464(4)	2892(3)	36(1)
C(13)	2885(5)	7948(3)	4126(3)	40(1)
C(14)	3440(4)	7370(3)	3033(3)	30(1)
C(15)	4658(5)	7976(3)	2468(3)	35(1)
C(16)	3759(4)	7295(3)	-30(3)	31(1)
C(17)	2901(4)	6480(3)	-467(4)	41(1)
C(18)	1621(6)	6557(5)	-1511(5)	63(1)
C(19)	6952(4)	7787(2)	872(3)	29(1)
C(20)	7088(4)	8002(3)	-337(4)	38(1)
C(21)	8420(5)	8473(4)	-636(5)	55(1)
C(22)	9612(5)	8733(4)	268(6)	65(2)
C(23)	9490(5)	8513(4)	1452(6)	67(2)
C(24)	8173(5)	8034(4)	1771(4)	50(1)

Table A21 Crystallographic Data for Complex **105c**

Empirical formula	$\text{C}_{24}\text{H}_{26}\text{Cl}_2\text{P}_2\text{Pd}$	
Formula weight	553.69	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	$a = 8.6882(3)$ Å	$\alpha = 67.228(2)^\circ$
	$b = 8.8228(3)$ Å	$\beta = 69.331(2)^\circ$
	$c = 9.1872(3)$ Å	$\gamma = 85.426(2)^\circ$
Volume	$606.23(4)$ Å ³	
Z	1	
Density (calculated)	1.517 Mg/m ³	
Absorption coefficient	1.126 mm ⁻¹	
F(000)	280	
Crystal size	0.25 x 0.08 x 0.06 mm ³	
Theta range for data collection	2.51 to 30.60°	
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -	
	13 ≤ l ≤ 13	
Reflections collected	12663	
Independent reflections	6128 [R(int) = 0.0219]	
Completeness to theta = 30.60°	97.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9355 and 0.7660	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6128 / 3 / 264	
Goodness-of-fit on F ²	1.047	
Final R indices [I > 2σ(I)]	R ₁ = 0.0251, wR ₂ = 0.0543	
R indices (all data)	R ₁ = 0.0281, wR ₂ = 0.0556	
Absolute structure parameter	-0.003(15)	
Largest diff. peak and hole	0.682 and -0.456 e.Å ⁻³	

Table A22 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex **105c**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	2829(1)	10548(1)	647(1)	20(1)
Cl(1)	-6(1)	9795(1)	1978(1)	38(1)
Cl(2)	2367(1)	12830(1)	-1550(1)	34(1)
P(1)	3233(1)	8266(1)	2634(1)	23(1)
P(2)	5580(1)	11062(1)	-333(1)	25(1)
C(1)	2125(3)	6424(3)	3008(3)	26(1)
C(2)	2707(4)	5651(4)	1853(4)	35(1)
C(3)	1791(4)	4330(4)	2029(4)	43(1)
C(4)	309(4)	3770(4)	3332(4)	43(1)
C(5)	-289(4)	4524(4)	4473(4)	43(1)
C(6)	616(4)	5851(4)	4310(4)	36(1)
C(7)	2676(3)	8477(3)	4640(3)	26(1)
C(8)	2601(4)	7125(4)	6114(3)	32(1)
C(9)	2157(4)	7330(4)	7629(4)	41(1)
C(10)	1786(4)	8862(5)	7696(4)	44(1)
C(11)	1846(4)	10206(4)	6253(4)	46(1)
C(12)	2293(4)	10012(4)	4733(4)	36(1)
C(13)	6046(4)	6558(4)	3222(4)	45(1)
C(14)	5464(3)	7887(4)	1913(4)	31(1)
C(15)	6400(3)	9559(4)	1194(4)	32(1)
C(16)	6586(4)	10762(4)	-2277(4)	35(1)
C(17)	5777(4)	10737(4)	-3248(4)	45(1)
C(18)	6561(6)	10527(6)	-4898(5)	71(1)
C(19)	6421(3)	13053(3)	-702(3)	26(1)
C(20)	7670(4)	13184(4)	-160(4)	42(1)
C(21)	8359(4)	14742(4)	-543(5)	48(1)
C(22)	7805(4)	16118(5)	-1427(5)	48(1)
C(23)	6551(5)	16028(4)	-1982(5)	53(1)
C(24)	5851(4)	14496(4)	-1627(4)	44(1)

Table A23 Crystallographic Data for Complex **108**

Empirical formula	$\text{C}_{28}\text{H}_{26}\text{Cl}_2\text{OP}_2\text{Pd}$	
Formula weight	617.73	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	$a = 17.3953(7)$ Å	$\alpha = 90^\circ$.
	$b = 8.7688(3)$ Å	$\beta = 104.198(3)^\circ$.
	$c = 18.2530(6)$ Å	$\gamma = 90^\circ$.
Volume	$2699.19(17)$ Å ³	
Z	4	
Density (calculated)	1.520 Mg/m ³	
Absorption coefficient	1.024 mm ⁻¹	
F(000)	1248	
Crystal size	0.20 x 0.20 x 0.15 mm ³	
Theta range for data collection	2.30 to 30.63°.	
Index ranges	$-24 \leq h \leq 24$, $-12 \leq k \leq 12$, $-$	
	$26 \leq l \leq 26$	
Reflections collected	34052	
Independent reflections	7955 [R(int) = 0.0317]	
Completeness to theta = 30.63°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8616 and 0.8215	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7955 / 2 / 308	
Goodness-of-fit on F ²	1.099	
Final R indices [I>2sigma(I)]	$R_1 = 0.0244$, $wR_2 = 0.0575$	
R indices (all data)	$R_1 = 0.0266$, $wR_2 = 0.0586$	
Absolute structure parameter	-0.019(13)	
Largest diff. peak and hole	0.826 and -0.518 e.Å ⁻³	

Table A24 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex **108**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	5001(1)	5926(1)	2500(1)	36(1)
Cl(1)	6189(1)	7221(1)	2523(1)	70(1)
Cl(2)	4671(1)	5610(1)	1179(1)	81(1)
O(1)	2913(1)	4588(3)	4426(1)	74(1)
P(1)	5125(1)	5878(1)	3747(1)	33(1)
P(2)	3930(1)	4705(1)	2659(1)	32(1)
C(1)	5116(1)	7632(2)	4268(1)	41(1)
C(2)	4682(2)	7743(3)	4815(1)	52(1)
C(3)	4721(2)	9079(3)	5236(2)	71(1)
C(4)	5189(3)	10272(3)	5114(2)	76(1)
C(5)	5598(3)	10170(3)	4574(2)	82(1)
C(6)	5579(2)	8855(3)	4140(2)	59(1)
C(7)	5943(1)	4760(2)	4288(1)	37(1)
C(8)	6052(2)	4572(3)	5064(1)	49(1)
C(9)	6690(2)	3719(3)	5472(2)	62(1)
C(10)	7216(2)	3082(3)	5116(2)	67(1)
C(11)	7125(2)	3271(3)	4362(2)	66(1)
C(12)	6490(2)	4108(3)	3931(2)	51(1)
C(13)	4155(1)	4930(2)	3706(1)	33(1)
C(14)	4096(1)	3544(3)	4197(1)	40(1)
C(15)	3309(2)	3465(3)	4417(2)	51(1)
C(16)	3082(3)	1948(4)	4663(3)	100(1)
C(17)	2968(1)	5529(2)	2247(1)	39(1)
C(18)	2442(2)	5854(4)	2679(2)	63(1)
C(19)	1719(2)	6557(5)	2340(2)	81(1)
C(20)	1531(2)	6926(4)	1599(2)	78(1)
C(21)	2031(2)	6565(6)	1166(2)	92(1)
C(22)	2758(2)	5836(4)	1483(2)	70(1)
C(23)	3885(1)	2685(2)	2442(1)	38(1)

C(24)	3200(2)	1872(3)	2412(2)	59(1)
C(25)	3191(2)	305(4)	2292(2)	79(1)
C(26)	3863(2)	-411(3)	2194(2)	76(1)
C(27)	4543(2)	376(3)	2229(2)	67(1)
C(28)	4562(2)	1948(3)	2349(2)	54(1)

Table A25 Crystallographic Data for Complex **110a**

Empirical formula	$C_{44}H_{47}ClNO_{5.50}P_2Pd$	
Formula weight	881.62	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2	
Unit cell dimensions	$a = 29.8157(17)$ Å	$\alpha = 90^\circ$.
	$b = 10.9192(6)$ Å	$\beta = 90^\circ$.
	$c = 13.2866(7)$ Å	$\gamma = 90^\circ$.
Volume	$4325.6(4)$ Å ³	
Z	4	
Density (calculated)	1.354 Mg/m ³	
Absorption coefficient	0.610 mm ⁻¹	
F(000)	1820	
Crystal size	$0.15 \times 0.05 \times 0.02$ mm ³	
Theta range for data collection	1.99 to 27.00° .	
Index ranges	$-37 \leq h \leq 36$, $-13 \leq k \leq 13$, $-16 \leq l \leq 16$	
Reflections collected	20653	
Independent reflections	8440 [R(int) = 0.1019]	
Completeness to $\theta = 25.00^\circ$	91.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9879 and 0.9141	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8440 / 2 / 497	
Goodness-of-fit on F ²	0.972	
Final R indices [I > 2σ(I)]	$R_1 = 0.0661$, $wR_2 = 0.1167$	
R indices (all data)	$R_1 = 0.1745$, $wR_2 = 0.1652$	
Absolute structure parameter	-0.02(6)	
Largest diff. peak and hole	0.460 and -0.395 e.Å ⁻³	

Table A26 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex **110a**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	8650(1)	7620(1)	1795(1)	48(1)
C(1)	9042(3)	8944(11)	1160(7)	54(3)
C(2)	9310(3)	9839(10)	1632(8)	59(3)
C(3)	9536(3)	10745(12)	1108(10)	76(3)
C(4)	9497(4)	10819(11)	63(10)	69(3)
C(5)	9725(4)	11743(12)	-503(11)	86(4)
C(6)	9705(4)	11806(15)	-1516(12)	112(6)
C(7)	9455(5)	10909(17)	-2022(10)	113(6)
C(8)	9224(4)	9931(15)	-1544(8)	94(4)
C(9)	9238(4)	9891(13)	-468(8)	74(4)
C(10)	9004(3)	8996(12)	118(8)	64(3)
C(11)	8729(4)	7980(12)	-405(7)	71(4)
C(12)	9031(4)	6875(12)	-634(8)	85(4)
C(13)	8111(4)	6600(14)	-34(8)	94(5)
C(14)	8027(4)	8711(13)	329(9)	84(4)
C(15)	8811(3)	6321(10)	4017(7)	48(3)
C(16)	8308(3)	6076(10)	3887(7)	50(3)
C(17)	8173(4)	4894(12)	4368(7)	59(3)
C(18)	7687(3)	4756(13)	4677(8)	86(4)
C(19)	8267(4)	4613(10)	2019(7)	51(3)
C(20)	8655(4)	4463(10)	1450(7)	62(3)
C(21)	8758(4)	3365(13)	1021(9)	87(4)
C(22)	8475(4)	2411(14)	1172(8)	83(4)
C(23)	8092(4)	2497(11)	1730(8)	76(3)
C(24)	7998(4)	3631(10)	2176(6)	58(3)
C(25)	7590(3)	6553(9)	2432(7)	47(2)
C(26)	7274(3)	5922(10)	1871(8)	66(3)
C(27)	6848(4)	6379(14)	1774(10)	86(4)

C(28)	6724(4)	7524(14)	2141(8)	81(3)
C(29)	7030(4)	8145(12)	2681(8)	82(4)
C(30)	7460(3)	7671(11)	2826(6)	63(3)
C(31)	9584(3)	7630(10)	3401(7)	54(2)
C(32)	9832(4)	8244(14)	4055(10)	107(5)
C(33)	10314(5)	8044(18)	4076(12)	129(7)
C(34)	10502(5)	7211(15)	3470(13)	110(5)
C(35)	10256(5)	6590(17)	2866(13)	126(7)
C(36)	9799(4)	6797(12)	2799(9)	86(4)
C(37)	8768(4)	8948(10)	4059(7)	57(3)
C(38)	8815(4)	8991(12)	5101(7)	80(4)
C(39)	8655(5)	10039(14)	5631(8)	91(4)
C(40)	8464(4)	11012(12)	5133(10)	78(4)
C(41)	8410(4)	10998(12)	4134(9)	77(4)
C(42)	8560(4)	9972(11)	3613(7)	68(3)
C(43)	9690(12)	4870(60)	6130(30)	390(30)
C(44)	9332(10)	4430(40)	6590(30)	340(20)
CI(1)	8129(2)	7017(3)	6869(3)	111(1)
N(1)	8350(2)	7688(10)	331(5)	58(2)
O(1)	8437(3)	4072(8)	4488(6)	82(3)
O(2)	8155(4)	8066(9)	7423(7)	136(4)
O(3)	7909(5)	7257(12)	5977(7)	188(6)
O(4)	7920(7)	6153(10)	7438(9)	235(10)
O(5)	8526(6)	6533(15)	6588(12)	259(9)
O(6)	10000	5000	6840(30)	380(30)
P(1)	8972(1)	7691(3)	3322(2)	49(1)
P(2)	8176(1)	6153(2)	2520(2)	45(1)

Table A27 Crystallographic Data for Complex **111**

Empirical formula	$\text{C}_{28}\text{H}_{26}\text{Cl}_2\text{OP}_2\text{Pd}\cdot\text{CH}_2\text{Cl}_2$	
Formula weight	702.65	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	$a = 14.6287(4)$ Å	$\alpha = 79.822(2)^\circ$.
	$b = 15.3517(4)$ Å	$\beta = 79.008(2)^\circ$.
	$c = 15.6590(4)$ Å	$\gamma = 64.276(2)^\circ$.
Volume	$3092.39(14)$ Å ³	
Z	4	
Density (calculated)	1.509 Mg/m ³	
Absorption coefficient	1.070 mm ⁻¹	
F(000)	1416	
Crystal size	$0.30 \times 0.08 \times 0.08$ mm ³	
Theta range for data collection	1.56 to 30.67° .	
Index ranges	$-20 \leq h \leq 20$, $-21 \leq k \leq 21$, $-$	
	$22 \leq l \leq 22$	
Reflections collected	82026	
Independent reflections	18917 [$R(\text{int}) = 0.0561$]	
Completeness to $\theta = 30.67^\circ$	98.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9193 and 0.7395	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	18917 / 0 / 669	
Goodness-of-fit on F^2	1.034	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0414$, $wR_2 = 0.0945$	
R indices (all data)	$R_1 = 0.0854$, $wR_2 = 0.1207$	
Largest diff. peak and hole	0.789 and -0.486 e.Å ⁻³	

Table A28 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex **111**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	2582(1)	8188(1)	3877(1)	32(1)
Pd(2)	3213(1)	7361(1)	-1065(1)	35(1)
O(1)	3962(2)	4932(2)	5981(2)	61(1)
O(2)	-137(2)	8826(3)	1145(2)	74(1)
P(1)	3598(1)	7992(1)	4859(1)	31(1)
P(2)	2268(1)	6974(1)	4691(1)	31(1)
P(3)	3138(1)	8266(1)	-66(1)	36(1)
P(4)	1838(1)	7219(1)	-264(1)	36(1)
Cl(1)	1476(1)	8285(1)	2913(1)	53(1)
Cl(2)	2850(1)	9554(1)	3151(1)	53(1)
Cl(3)	3150(1)	6481(1)	-2121(1)	58(1)
Cl(4)	4766(1)	7411(1)	-1743(1)	55(1)
Cl(5)	9878(2)	5426(3)	8025(2)	233(2)
Cl(6)	10049(2)	4819(2)	6367(2)	166(1)
Cl(7)	3834(1)	1652(1)	3752(1)	77(1)
Cl(8)	2887(1)	2020(1)	2192(1)	122(1)
C(1)	3915(2)	6778(2)	5444(2)	35(1)
C(2)	2936(2)	6626(2)	5691(2)	34(1)
C(3)	3136(3)	5589(3)	6108(2)	44(1)
C(4)	2245(3)	5454(3)	6683(3)	65(1)
C(5)	920(3)	7334(2)	5070(2)	43(1)
C(6)	317(3)	7120(3)	4646(3)	57(1)
C(7)	-736(4)	7477(4)	4897(4)	88(2)
C(8)	-1166(4)	8076(5)	5585(4)	102(2)
C(9)	-576(4)	8283(4)	5990(3)	91(2)
C(10)	457(3)	7926(3)	5748(3)	66(1)

C(11)	2736(2)	5884(2)	4150(2)	36(1)
C(12)	3492(3)	5753(3)	3438(2)	54(1)
C(13)	3920(3)	4899(3)	3050(3)	69(1)
C(14)	3577(4)	4185(3)	3356(3)	66(1)
C(15)	2828(3)	4301(3)	4046(3)	62(1)
C(16)	2401(3)	5146(2)	4457(2)	48(1)
C(17)	2906(2)	8833(2)	5677(2)	35(1)
C(18)	1928(3)	9525(2)	5589(2)	53(1)
C(19)	1368(3)	10131(3)	6248(3)	66(1)
C(20)	1815(4)	10045(3)	6976(2)	62(1)
C(21)	2789(3)	9362(3)	7063(2)	59(1)
C(22)	3337(3)	8750(3)	6421(2)	45(1)
C(23)	4789(2)	8107(2)	4464(2)	36(1)
C(24)	5673(3)	7325(3)	4197(3)	55(1)
C(25)	6548(3)	7437(3)	3854(3)	73(1)
C(26)	6582(3)	8328(3)	3769(3)	65(1)
C(27)	5714(3)	9112(3)	4022(3)	62(1)
C(28)	4820(3)	9013(3)	4363(2)	49(1)
C(29)	1862(2)	8648(2)	561(2)	42(1)
C(30)	1603(2)	7762(2)	780(2)	40(1)
C(31)	517(3)	8026(3)	1261(2)	56(1)
C(32)	326(4)	7220(4)	1856(3)	84(2)
C(33)	2033(3)	5951(2)	21(2)	45(1)
C(34)	1681(4)	5515(3)	-466(3)	67(1)
C(35)	1909(5)	4543(4)	-298(4)	90(2)
C(36)	2502(5)	3982(4)	341(4)	93(2)
C(37)	2865(4)	4394(4)	819(3)	84(2)
C(38)	2633(3)	5379(3)	669(3)	62(1)
C(39)	674(3)	7854(2)	-767(2)	41(1)
C(40)	636(3)	8574(3)	-1451(2)	56(1)
C(41)	-261(4)	9108(3)	-1825(3)	72(1)

C(42)	-1099(4)	8922(3)	-1539(3)	74(1)
C(43)	-1074(3)	8203(4)	-870(3)	73(1)
C(44)	-191(3)	7675(3)	-472(2)	58(1)
C(45)	4028(2)	7581(3)	721(2)	43(1)
C(46)	4682(3)	6621(3)	633(2)	59(1)
C(47)	5342(3)	6091(4)	1255(3)	81(2)
C(48)	5348(3)	6533(4)	1947(3)	80(2)
C(49)	4703(3)	7484(4)	2035(2)	69(1)
C(50)	4036(3)	8018(3)	1420(2)	53(1)
C(51)	3341(3)	9354(2)	-489(2)	43(1)
C(52)	4318(4)	9331(3)	-594(3)	66(1)
C(53)	4475(4)	10154(4)	-981(3)	82(2)
C(54)	3684(5)	10975(4)	-1274(3)	91(2)
C(55)	2732(5)	11000(3)	-1176(3)	86(2)
C(56)	2546(3)	10197(3)	-786(2)	62(1)
C(57)	9331(7)	5601(7)	7127(6)	160(3)
C(58)	3914(4)	1262(3)	2742(3)	76(1)

Table A29 Crystallographic Data for Complex **113a**

Empirical formula	$\text{C}_{43}\text{H}_{44}\text{ClNO}_6\text{P}_2\text{Pd} \cdot 0.5\text{CH}_2\text{Cl}_2$	
Formula weight	917.05	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	$a = 19.6133(8)$ Å	$\alpha = 90^\circ$.
	$b = 9.4188(3)$ Å	$\beta = 107.688(2)^\circ$.
	$c = 23.1706(9)$ Å	$\gamma = 90^\circ$.
Volume	4078.0(3) Å ³	
Z	4	
Density (calculated)	1.494 Mg/m ³	
Absorption coefficient	0.714 mm ⁻¹	
F(000)	1884	
Crystal size	0.25 x 0.25 x 0.10 mm ³	
Theta range for data collection	0.92 to 30.54°.	
Index ranges	-27 ≤ h ≤ 24, -13 ≤ k ≤ 13, -	
	32 ≤ l ≤ 32	
Reflections collected	53802	
Independent reflections	20305 [R(int) = 0.0362]	
Completeness to theta = 30.54°	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9320 and 0.8417	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	20305 / 1 / 1008	
Goodness-of-fit on F ²	1.150	
Final R indices [I > 2σ(I)]	R ₁ = 0.0540, wR ₂ = 0.1564	
R indices (all data)	R ₁ = 0.0689, wR ₂ = 0.1794	
Absolute structure parameter	0.01(3)	
Largest diff. peak and hole	1.686 and -1.666 e.Å ⁻³	

Table A30 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex **113a**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	2913(1)	4802(1)	2385(1)	20(1)
Pd(2)	2171(1)	9803(1)	7538(1)	18(1)
N(1)	2470(3)	6692(6)	2662(2)	34(1)
N(2)	2639(3)	11547(5)	7173(2)	23(1)
P(1)	3816(1)	4250(2)	3306(1)	22(1)
P(2)	3311(1)	2824(1)	2053(1)	19(1)
P(3)	1217(1)	9138(2)	6663(1)	19(1)
P(4)	1776(1)	7922(1)	7951(1)	19(1)
C(1)	2130(3)	5311(6)	1590(2)	20(1)
C(2)	2070(3)	4926(7)	984(2)	24(1)
C(3)	1529(3)	5438(6)	504(2)	26(1)
C(4)	1008(3)	6392(6)	594(2)	24(1)
C(5)	450(3)	6924(7)	108(3)	31(1)
C(6)	-39(3)	7879(7)	193(3)	35(2)
C(7)	25(3)	8331(7)	793(3)	32(1)
C(8)	541(3)	7801(6)	1278(3)	29(1)
C(9)	1064(3)	6814(6)	1195(2)	23(1)
C(10)	1625(3)	6212(6)	1685(2)	23(1)
C(11)	1685(3)	6536(7)	2341(3)	30(1)
C(12)	1345(4)	5324(8)	2602(3)	36(1)
C(13)	2602(4)	6912(9)	3318(3)	47(2)
C(14)	2734(4)	8016(7)	2427(4)	46(2)
C(15)	3522(3)	4166(6)	3979(2)	24(1)
C(16)	3788(3)	5010(6)	4487(2)	28(1)
C(17)	3513(3)	4964(8)	4966(3)	35(1)
C(18)	2935(4)	4033(9)	4937(3)	40(2)
C(19)	2655(4)	3174(10)	4428(3)	46(2)
C(20)	2953(4)	3253(8)	3952(3)	35(1)
C(21)	4554(3)	5458(6)	3459(2)	26(1)
C(22)	4504(3)	6575(7)	3047(3)	30(1)
C(23)	5015(4)	7666(8)	3156(3)	40(2)
C(24)	5601(4)	7614(9)	3677(3)	45(2)
C(25)	5685(4)	6477(10)	4075(3)	47(2)
C(26)	5161(4)	5410(9)	3971(3)	41(2)
C(27)	4178(3)	2445(6)	3232(2)	25(1)
C(28)	4423(4)	1634(8)	3831(3)	35(2)
C(29)	4298(5)	-645(10)	4295(4)	58(2)
C(30)	3685(5)	-680(10)	4535(3)	51(2)
C(31)	3643(3)	1653(6)	2711(2)	22(1)

C(32)	2718(3)	1681(6)	1491(2)	24(1)
C(33)	2976(4)	836(8)	1104(3)	39(2)
C(34)	2509(4)	-51(10)	691(3)	49(2)
C(35)	1799(4)	-97(9)	648(3)	45(2)
C(36)	1545(4)	696(8)	1028(4)	44(2)
C(37)	1996(3)	1609(7)	1446(3)	31(1)
C(38)	4068(3)	3125(6)	1773(2)	20(1)
C(39)	4648(3)	2201(6)	1901(3)	27(1)
C(40)	5200(3)	2427(7)	1644(3)	30(1)
C(41)	5192(3)	3579(7)	1273(3)	30(1)
C(42)	4610(3)	4555(7)	1156(2)	29(1)
C(43)	4063(3)	4348(6)	1407(3)	26(1)
C(44)	2968(3)	10444(5)	8302(2)	20(1)
C(45)	3016(3)	10216(6)	8919(2)	24(1)
C(46)	3533(3)	10839(6)	9388(2)	22(1)
C(47)	4069(3)	11695(6)	9262(2)	26(1)
C(48)	4627(3)	12324(7)	9734(3)	32(1)
C(49)	5140(4)	13137(8)	9613(3)	38(2)
C(50)	5112(3)	13429(7)	9003(3)	33(1)
C(51)	4581(3)	12826(6)	8535(3)	26(1)
C(52)	4042(3)	11948(6)	8649(2)	23(1)
C(53)	3477(3)	11304(6)	8177(2)	23(1)
C(54)	3430(3)	11466(6)	7516(2)	22(1)
C(55)	3806(4)	10241(7)	7318(3)	30(1)
C(56)	2348(3)	12925(7)	7311(3)	37(2)
C(57)	2536(4)	11532(8)	6509(3)	36(2)
C(58)	459(3)	10291(6)	6543(2)	24(1)
C(59)	514(3)	11426(6)	6949(3)	27(1)
C(60)	-32(4)	12428(7)	6866(3)	37(2)
C(61)	-644(4)	12282(8)	6384(3)	38(2)
C(62)	-729(4)	11149(9)	5997(3)	41(2)
C(63)	-180(3)	10126(8)	6071(3)	36(2)
C(64)	1429(3)	9022(6)	5948(2)	22(1)
C(65)	1131(3)	9895(8)	5452(2)	28(1)
C(66)	1370(3)	9868(9)	4955(2)	35(1)
C(67)	1931(4)	8928(8)	4945(3)	38(2)
C(68)	2220(4)	8013(8)	5431(3)	36(1)
C(69)	1972(3)	8066(7)	5940(3)	33(1)
C(70)	901(3)	7337(6)	6804(2)	23(1)
C(71)	638(3)	6414(6)	6235(3)	28(1)
C(72)	729(4)	4115(9)	5803(4)	47(2)
C(73)	1266(5)	4245(10)	5484(4)	53(2)
C(74)	1470(3)	6616(5)	7331(2)	21(1)
C(75)	2395(3)	6971(6)	8575(2)	22(1)
C(76)	2306(3)	6940(7)	9157(3)	32(1)
C(77)	2822(4)	6298(8)	9637(3)	38(2)

C(78)	3407(4)	5667(7)	9550(3)	38(2)
C(79)	3499(3)	5668(7)	8979(3)	32(1)
C(80)	3005(3)	6349(7)	8500(3)	28(1)
C(81)	1009(3)	8235(6)	8211(2)	20(1)
C(82)	454(3)	7255(6)	8121(3)	27(1)
C(83)	-109(3)	7510(7)	8358(3)	28(1)
C(84)	-121(3)	8707(7)	8698(3)	30(1)
C(85)	438(3)	9699(8)	8795(3)	34(1)
C(86)	989(3)	9479(6)	8543(3)	30(1)
C(87)	2017(4)	3210(8)	8879(3)	46(2)
CI(1)	3624(1)	5953(1)	6857(1)	26(1)
CI(2)	8670(1)	5874(2)	6938(1)	30(1)
CI(3)	1177(1)	3467(3)	8328(1)	55(1)
CI(4)	1930(1)	2545(3)	9561(1)	54(1)
O(1)	4835(3)	2087(6)	4288(2)	50(1)
O(2)	4140(3)	321(6)	3766(2)	46(1)
O(3)	930(3)	5116(5)	6318(2)	44(1)
O(4)	211(3)	6822(5)	5773(2)	37(1)
O(5)	3159(3)	5168(5)	6359(2)	43(1)
O(6)	3189(3)	6755(6)	7135(2)	41(1)
O(7)	4054(3)	4987(6)	7294(2)	58(2)
O(8)	4074(3)	6869(9)	6641(3)	69(2)
O(9)	8201(3)	5129(6)	6430(2)	54(2)
O(10)	8243(4)	6661(8)	7235(3)	73(2)
O(11)	9099(3)	4891(7)	7362(2)	58(1)
O(12)	9107(4)	6825(12)	6738(3)	105(4)

Table A31 Crystallographic Data for Complex **114**

Empirical formula	$\text{C}_{29}\text{H}_{28}\text{Cl}_2\text{O}_2\text{P}_2\text{Pd}$	
Formula weight	647.75	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	$a = 8.4679(4)$ Å	$\alpha = 108.270(3)^\circ$.
	$b = 9.4313(4)$ Å	$\beta = 95.700(3)^\circ$.
	$c = 9.8768(5)$ Å	$\gamma = 106.962(2)^\circ$.
Volume	$700.46(6)$ Å ³	
Z	1	
Density (calculated)	1.536 Mg/m ³	
Absorption coefficient	0.992 mm ⁻¹	
F(000)	328	
Crystal size	0.25 x 0.20 x 0.10 mm ³	
Theta range for data collection	2.22 to 30.49°.	
Index ranges	-11 ≤ h ≤ 12, -13 ≤ k ≤ 13, -	
	12 ≤ l ≤ 14	
Reflections collected	12896	
Independent reflections	7112 [R(int) = 0.0171]	
Completeness to theta = 30.49°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9073 and 0.7895	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7112 / 43 / 346	
Goodness-of-fit on F ²	1.008	
Final R indices [I > 2σ(I)]	R ₁ = 0.0179, wR ₂ = 0.0428	
R indices (all data)	R ₁ = 0.0183, wR ₂ = 0.0430	
Absolute structure parameter	-0.022(9)	
Largest diff. peak and hole	0.517 and -0.291 e.Å ⁻³	

Table A32 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex **114**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	-1447(1)	9369(1)	9675(1)	19(1)
Cl(1)	-4386(1)	8074(1)	8838(1)	36(1)
Cl(2)	-1670(1)	11366(1)	11726(1)	31(1)
P(1)	-1051(1)	7355(1)	7982(1)	20(1)
P(2)	1356(1)	10524(1)	10221(1)	18(1)
C(1)	-1927(2)	5460(2)	8188(2)	25(1)
C(2)	-1090(3)	5143(3)	9294(3)	34(1)
C(3)	-1723(3)	3704(3)	9485(3)	45(1)
C(4)	-3208(3)	2559(3)	8573(3)	48(1)
C(5)	-4080(3)	2874(3)	7507(3)	48(1)
C(6)	-3455(3)	4334(2)	7311(3)	36(1)
C(7)	-1733(2)	7097(2)	6096(2)	27(1)
C(8)	-1891(3)	5709(3)	4950(2)	35(1)
C(9)	-2271(3)	5579(3)	3503(3)	46(1)
C(10)	-2504(3)	6848(4)	3197(3)	48(1)
C(11)	-2363(3)	8218(3)	4305(3)	48(1)
C(12)	-1984(3)	8368(3)	5771(3)	37(1)
C(13)	1293(2)	7769(2)	8221(2)	20(1)
C(14)	1745(2)	6832(2)	6861(2)	24(1)
C(15)	1427(19)	4168(11)	5448(14)	45(2)
C(16)	530(30)	2520(11)	5535(13)	66(3)
C(15A)	1870(30)	4359(13)	5484(13)	45(3)
C(16A)	1410(40)	2736(16)	5511(12)	70(5)
C(17)	2173(2)	9554(2)	8671(2)	22(1)
C(18)	2312(2)	10177(2)	11754(2)	21(1)
C(19)	4064(2)	10781(2)	12248(2)	29(1)
C(20)	4786(2)	10482(3)	13405(2)	34(1)
C(21)	3771(2)	9581(2)	14074(2)	29(1)
C(22)	2039(2)	8974(2)	13585(2)	29(1)

C(23)	1301(2)	9277(2)	12432(2)	25(1)
C(24)	2225(2)	12634(2)	10588(2)	21(1)
C(25)	2658(3)	13209(2)	9498(2)	37(1)
C(26)	3292(3)	14841(2)	9807(3)	41(1)
C(27)	3455(2)	15888(2)	11167(2)	33(1)
C(28)	3030(3)	15329(2)	12277(3)	42(1)
C(29)	2433(3)	13705(2)	11981(3)	39(1)
O(1)	1378(2)	5320(2)	6775(2)	34(1)
O(2)	2294(2)	7353(2)	5977(2)	35(1)

Table A33 Crystallographic Data for Complex **119**

Empirical formula	$\text{C}_{29}\text{H}_{28}\text{Cl}_2\text{O}_2\text{P}_2\text{Pd}$
Formula weight	647.75
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	$a = 20.6239(7)$ Å $\alpha = 90^\circ$. $b = 16.0221(5)$ Å $\beta = 110.173(2)^\circ$. $c = 18.0126(5)$ Å $\gamma = 90^\circ$.
Volume	$5586.9(3)$ Å ³
Z	8
Density (calculated)	1.540 Mg/m ³
Absorption coefficient	0.995 mm ⁻¹
F(000)	2624
Crystal size	0.25 x 0.25 x 0.25 mm ³
Theta range for data collection	1.05 to 30.64°.
Index ranges	-23 ≤ h ≤ 29, -22 ≤ k ≤ 22, - 25 ≤ l ≤ 22
Reflections collected	68179
Independent reflections	17094 [R(int) = 0.0521]
Completeness to theta = 30.64°	99.1 %
Absorption correction	None
Max. and min. transmission	0.7889 and 0.7889
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	17094 / 0 / 651
Goodness-of-fit on F ²	1.069
Final R indices [I > 2σ(I)]	R ₁ = 0.0408, wR ₂ = 0.0944
R indices (all data)	R ₁ = 0.0658, wR ₂ = 0.1284
Largest diff. peak and hole	2.058 and -1.646 e.Å ⁻³

Table A34 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex **119**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	9356(1)	18(1)	7232(1)	22(1)
Pd(2)	4404(1)	-641(1)	2031(1)	21(1)
Cl(1)	8525(1)	-1015(1)	6629(1)	38(1)
Cl(2)	10019(1)	-881(1)	8251(1)	37(1)
Cl(3)	3848(1)	-1692(1)	1120(1)	38(1)
Cl(4)	4908(1)	-1620(1)	3058(1)	32(1)
P(1)	8831(1)	986(1)	6347(1)	19(1)
P(2)	9989(1)	1178(1)	7613(1)	20(1)
P(3)	3903(1)	408(1)	1224(1)	20(1)
P(4)	4860(1)	520(1)	2694(1)	23(1)
C(1)	8933(2)	847(2)	5395(2)	25(1)
C(2)	8922(3)	50(3)	5090(3)	40(1)
C(3)	9037(3)	-60(3)	4380(3)	48(1)
C(4)	9158(2)	618(3)	3974(3)	44(1)
C(5)	9159(2)	1414(3)	4267(2)	39(1)
C(6)	9051(2)	1532(2)	4979(2)	31(1)
C(7)	7947(2)	1217(2)	6236(2)	22(1)
C(8)	7469(2)	1485(2)	5520(2)	32(1)
C(9)	6813(2)	1743(3)	5490(3)	47(1)
C(10)	6636(2)	1727(3)	6161(3)	45(1)
C(11)	7106(2)	1450(3)	6874(3)	37(1)
C(12)	7760(2)	1192(2)	6912(2)	29(1)
C(13)	9387(2)	1881(2)	6855(2)	22(1)
C(14)	9047(2)	2548(2)	7214(2)	27(1)
C(15)	8494(2)	3089(2)	6630(2)	29(1)
C(16)	7986(2)	3557(3)	5318(3)	45(1)
C(17)	8029(2)	3405(3)	4519(3)	49(1)
C(18)	10129(2)	1569(2)	8601(2)	25(1)
C(19)	9819(2)	1165(3)	9078(2)	32(1)
C(20)	9957(2)	1439(3)	9848(2)	41(1)

C(21)	10394(3)	2111(3)	10134(2)	48(1)
C(22)	10695(3)	2520(3)	9659(3)	44(1)
C(23)	10558(2)	2248(2)	8885(2)	33(1)
C(24)	10830(2)	1219(2)	7514(2)	23(1)
C(25)	11071(2)	1934(2)	7246(2)	27(1)
C(26)	11745(2)	1949(3)	7242(2)	33(1)
C(27)	12173(2)	1262(3)	7504(2)	36(1)
C(28)	11937(2)	564(3)	7781(3)	35(1)
C(29)	11264(2)	535(2)	7787(2)	28(1)
C(30)	2995(2)	489(2)	1104(2)	23(1)
C(31)	2823(2)	406(2)	1788(2)	31(1)
C(32)	2143(2)	512(3)	1749(3)	38(1)
C(33)	1630(2)	668(3)	1032(3)	41(1)
C(34)	1795(2)	731(3)	346(3)	39(1)
C(35)	2480(2)	650(2)	386(2)	29(1)
C(36)	4011(2)	468(2)	269(2)	25(1)
C(37)	3674(2)	-115(3)	-301(2)	36(1)
C(38)	3756(2)	-86(3)	-1037(3)	47(1)
C(39)	4177(3)	511(4)	-1190(3)	50(1)
C(40)	4528(3)	1065(3)	-617(3)	50(1)
C(41)	4449(2)	1055(3)	118(3)	39(1)
C(42)	4376(2)	1271(2)	1891(2)	25(1)
C(43)	3960(2)	1946(2)	2125(2)	30(1)
C(44)	3464(2)	2465(2)	1470(3)	34(1)
C(45)	2950(2)	2742(3)	98(3)	44(1)
C(46)	2994(3)	2464(3)	-676(3)	51(1)
C(47)	4679(2)	733(2)	3587(2)	27(1)
C(48)	4249(2)	196(2)	3817(2)	31(1)
C(49)	4100(2)	365(3)	4493(3)	40(1)
C(50)	4389(2)	1052(3)	4949(3)	45(1)
C(51)	4818(2)	1586(3)	4723(3)	43(1)
C(52)	4966(2)	1442(3)	4038(3)	37(1)
C(53)	5776(2)	679(2)	2927(2)	24(1)
C(54)	6051(2)	1432(2)	2784(3)	34(1)
C(55)	6760(2)	1510(3)	2977(3)	42(1)
C(56)	7196(2)	857(3)	3327(3)	41(1)

C(57)	6931(2)	116(3)	3483(3)	40(1)
C(58)	6220(2)	22(2)	3284(2)	32(1)
O(1)	8490(1)	3019(2)	5891(2)	32(1)
O(2)	8124(2)	3535(2)	6837(2)	51(1)
O(3)	3474(1)	2290(2)	746(2)	34(1)
O(4)	3101(2)	2982(2)	1603(2)	64(1)

Table A35 Crystallographic Data for Complex **127d**

Empirical formula	$\text{C}_{46.50}\text{H}_{45}\text{Cl}_4\text{NO}_5\text{P}_2\text{Pd}$	
Formula weight	1007.98	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	$a = 15.9922(9)$ Å	$\alpha = 90^\circ$.
	$b = 14.0045(8)$ Å	$\beta = 108.093(3)^\circ$.
	$c = 20.9251(11)$ Å	$\gamma = 90^\circ$.
Volume	$4454.7(4)$ Å ³	
Z	4	
Density (calculated)	1.503 Mg/m ³	
Absorption coefficient	0.776 mm ⁻¹	
F(000)	2060	
Crystal size	0.25 x 0.20 x 0.10 mm ³	
Theta range for data collection	1.02 to 25.50°.	
Index ranges	$-19 \leq h \leq 19$, $-14 \leq k \leq 16$, $-$	
	$25 \leq l \leq 25$	
Reflections collected	60148	
Independent reflections	15392 [R(int) = 0.0462]	
Completeness to theta = 25.50°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9265 and 0.8297	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	15392 / 56 / 1080	
Goodness-of-fit on F ²	1.115	
Final R indices [I > 2σ(I)]	$R_1 = 0.0632$, $wR_2 = 0.1713$	
R indices (all data)	$R_1 = 0.0822$, $wR_2 = 0.1934$	
Absolute structure parameter	-0.02(4)	
Largest diff. peak and hole	2.148 and -1.116 e.Å ⁻³	

Table A36 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex **127d**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Cl(5)	5060(10)	8821(15)	8767(9)	395(13)
Cl(7)	4461(7)	6749(13)	10108(5)	336(9)
Pd(1)	7146(1)	2268(1)	5327(1)	26(1)
Pd(2)	7851(1)	7821(1)	9284(1)	30(1)
P(1)	7328(1)	2199(2)	4239(1)	27(1)
P(2)	8602(1)	2464(2)	5799(1)	29(1)
P(3)	7928(2)	7513(2)	8188(1)	28(1)
P(4)	7871(2)	6258(2)	9519(1)	29(1)
C(1)	6977(5)	2167(7)	6264(4)	26(2)
C(2)	7595(6)	1963(7)	6903(4)	36(2)
C(3)	7359(6)	1905(7)	7477(4)	33(2)
C(4)	6482(6)	2008(7)	7453(4)	35(2)
C(5)	6221(6)	1952(7)	8050(4)	38(2)
C(6)	5381(7)	2004(8)	8013(5)	44(3)
C(7)	4713(6)	2142(8)	7402(5)	43(2)
C(8)	4932(5)	2211(8)	6815(4)	33(2)
C(9)	5815(5)	2173(7)	6821(4)	28(2)
C(10)	6099(5)	2280(7)	6242(4)	28(2)
C(11)	5454(6)	2583(6)	5569(4)	29(2)
C(12)	5438(7)	3667(7)	5514(4)	37(2)
C(13)	5514(6)	1067(7)	5028(5)	37(2)
C(14)	5192(6)	2492(8)	4353(4)	40(2)
C(15)	6657(6)	1242(7)	3742(5)	33(2)
C(16)	6794(7)	301(8)	4009(5)	39(2)
C(17)	6254(7)	-419(8)	3678(6)	44(2)
C(18)	5561(8)	-249(9)	3096(6)	54(3)
C(19)	5412(7)	644(9)	2843(5)	49(3)
C(20)	5962(6)	1403(7)	3161(4)	35(2)
C(21)	7083(6)	3254(7)	3713(5)	38(2)

C(22)	7210(7)	3251(9)	3074(5)	48(3)
C(23)	7045(9)	4084(10)	2667(6)	63(4)
C(24)	6744(9)	4894(11)	2906(8)	71(4)
C(25)	6627(9)	4917(10)	3549(8)	68(4)
C(26)	6787(7)	4087(8)	3948(6)	44(3)
C(27)	8435(6)	1831(7)	4220(4)	34(2)
C(28)	8546(7)	1155(8)	3788(5)	40(2)
C(29)	9351(7)	841(8)	3773(5)	45(3)
C(30)	10101(7)	1227(8)	4224(5)	45(2)
C(31)	10011(6)	1937(8)	4658(5)	40(2)
C(32)	9185(5)	2254(8)	4671(4)	34(2)
C(33)	9145(6)	2980(8)	5190(5)	39(2)
C(34)	8971(5)	3328(7)	6487(4)	30(2)
C(35)	9674(7)	3149(8)	7062(5)	46(3)
C(36)	9952(8)	3856(10)	7554(6)	65(4)
C(37)	9544(8)	4759(10)	7462(6)	59(3)
C(38)	8845(7)	4938(8)	6876(5)	45(3)
C(39)	8559(7)	4215(8)	6400(5)	40(2)
C(40)	9175(6)	1326(7)	6027(4)	34(2)
C(41)	8669(7)	501(8)	5909(5)	46(3)
C(42)	9095(8)	-383(10)	5975(7)	61(3)
C(43)	9986(9)	-441(10)	6152(7)	64(3)
C(44)	10484(8)	383(10)	6254(7)	59(3)
C(45)	10076(7)	1274(8)	6193(6)	47(3)
C(46)	7612(6)	8147(8)	10186(4)	36(2)
C(47)	7081(6)	7651(8)	10493(5)	43(2)
C(48)	6895(7)	8029(9)	11028(5)	49(3)
C(49)	7233(7)	8895(9)	11307(5)	46(3)
C(50)	7014(8)	9323(11)	11862(5)	60(3)
C(51)	7362(10)	10185(12)	12110(6)	76(4)
C(52)	7899(10)	10696(11)	11826(6)	70(4)
C(53)	8113(10)	10348(10)	11282(6)	64(3)
C(54)	7764(7)	9439(8)	10998(5)	41(2)
C(55)	7919(6)	9034(8)	10400(4)	37(2)
C(56)	8441(8)	9573(8)	10034(5)	50(3)
C(57)	9402(8)	9301(9)	10270(6)	55(3)

C(58)	7140(9)	9817(9)	9079(5)	61(3)
C(59)	8550(11)	9796(9)	8906(6)	68(4)
C(60)	7076(6)	8274(7)	7617(4)	33(2)
C(61)	6224(7)	8197(7)	7654(5)	41(2)
C(62)	5567(7)	8799(8)	7277(6)	50(3)
C(63)	5758(8)	9489(8)	6871(6)	53(3)
C(64)	6582(8)	9571(8)	6857(6)	49(3)
C(65)	7255(7)	8978(7)	7210(4)	36(2)
C(66)	8920(6)	7679(7)	7949(4)	33(2)
C(67)	9709(6)	7904(8)	8439(5)	40(2)
C(68)	10475(8)	7966(11)	8279(6)	60(3)
C(69)	10453(8)	7822(10)	7596(6)	59(3)
C(70)	9695(7)	7629(8)	7131(5)	49(3)
C(71)	8905(7)	7542(7)	7284(5)	41(2)
C(72)	7549(5)	6340(7)	7870(4)	28(2)
C(73)	7012(6)	6203(7)	7205(4)	31(2)
C(74)	6737(6)	5290(7)	6957(5)	37(2)
C(75)	6983(7)	4489(8)	7358(5)	42(2)
C(76)	7537(6)	4599(7)	8013(4)	32(2)
C(77)	7834(6)	5500(7)	8277(4)	30(2)
C(78)	8432(6)	5586(7)	8993(4)	30(2)
C(79)	8505(6)	6011(7)	10383(4)	35(2)
C(80)	8192(8)	5426(9)	10791(6)	51(3)
C(81)	8674(10)	5313(10)	11487(6)	68(4)
C(82)	9437(9)	5768(10)	11752(5)	59(3)
C(83)	9771(8)	6327(10)	11351(6)	62(3)
C(84)	9290(7)	6478(9)	10652(5)	50(3)
C(85)	6825(6)	5618(7)	9334(5)	35(2)
C(86)	6060(7)	6109(9)	9117(5)	47(3)
C(87)	5239(8)	5599(13)	8922(6)	69(4)
C(88)	5257(9)	4623(12)	8986(6)	69(4)
C(89)	6064(9)	4126(11)	9226(6)	62(3)
C(90)	6826(8)	4613(8)	9393(5)	48(3)
C(91)	2237(9)	2525(12)	6486(6)	85(5)
C(92)	4904(16)	9740(20)	9266(16)	290(20)
C(93)	3554(17)	6930(20)	9434(12)	262(17)

Cl(1)	1421(2)	7539(2)	258(1)	45(1)
Cl(2)	7296(2)	6559(4)	5148(2)	97(2)
Cl(3)	2145(2)	2159(3)	7263(2)	74(1)
Cl(4)	1590(2)	3525(3)	6160(2)	91(1)
Cl(6)	3968(5)	10430(6)	8976(4)	152(3)
Cl(8)	3364(10)	7756(11)	8812(9)	350(10)
N(1)	5725(4)	2104(6)	5017(3)	28(2)
N(2)	8009(6)	9350(6)	9295(4)	42(2)
O(1)	8653(5)	3780(5)	4871(4)	47(2)
O(2)	9196(4)	6073(5)	8973(3)	36(2)
O(3)	1197(6)	8458(6)	-50(4)	65(2)
O(4)	803(5)	6850(6)	-109(4)	51(2)
O(5)	1362(8)	7606(10)	936(4)	107(4)
O(6)	2265(5)	7278(9)	334(6)	90(3)
O(7)	6788(7)	7154(13)	4633(5)	121(5)
O(8)	7828(11)	7077(17)	5672(7)	191(10)
O(9)	6730(10)	5856(18)	5243(11)	185(9)
O(10)	7910(7)	6033(13)	4882(7)	125(5)

Table A37 Crystallographic Data for Complex **128a** and **128b**

Empirical formula	$C_{31}H_{26}Cl_2OP_2Pd$	
Formula weight	653.76	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	$a = 7.7434(3)$ Å	$\alpha = 90^\circ$.
	$b = 20.2922(7)$ Å	$\beta = 93.999(2)^\circ$.
	$c = 17.8480(6)$ Å	$\gamma = 90^\circ$.
Volume	$2797.64(17)$ Å ³	
Z	4	
Density (calculated)	1.552 Mg/m ³	
Absorption coefficient	0.992 mm ⁻¹	
F(000)	1320	
Crystal size	0.16 x 0.12 x 0.08 mm ³	
Theta range for data collection	1.14 to 28.10°.	
Index ranges	-10 ≤ h ≤ 8, -26 ≤ k ≤ 24, -23 ≤ l ≤ 23	
Reflections collected	27316	
Independent reflections	12225 [R(int) = 0.0419]	
Completeness to theta = 28.10°	97.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9248 and 0.8574	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	12225 / 16 / 669	
Goodness-of-fit on F ²	1.073	
Final R indices [I > 2σ(I)]	R ₁ = 0.0407, wR ₂ = 0.0875	
R indices (all data)	R ₁ = 0.0556, wR ₂ = 0.1043	
Absolute structure parameter	-0.01(3)	
Largest diff. peak and hole	1.033 and -0.704 e.Å ⁻³	

Table A38 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex **128a** and **128b**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	-316(1)	5524(1)	240(1)	23(1)
Pd(2)	-306(1)	7196(1)	5169(1)	24(1)
C(1)	2259(8)	6840(3)	883(3)	25(1)
C(2)	1383(9)	7307(3)	450(4)	39(2)
C(3)	2195(10)	7904(4)	320(4)	43(2)
C(4)	3867(9)	8015(4)	599(4)	41(2)
C(5)	4771(10)	7541(4)	998(4)	42(2)
C(6)	3965(9)	6946(3)	1139(4)	35(2)
C(7)	-450(8)	6452(3)	1791(3)	26(1)
C(8)	-118(8)	7055(3)	2173(3)	33(1)
C(9)	-1134(8)	7243(3)	2736(3)	37(1)
C(10)	-2453(8)	6851(3)	2942(3)	35(2)
C(11)	-2827(8)	6271(4)	2565(3)	36(2)
C(12)	-1825(8)	6075(3)	1995(3)	29(1)
C(13)	2508(7)	5636(3)	1800(3)	23(1)
C(14)	2382(8)	5695(3)	2581(3)	31(1)
C(15)	3329(8)	5288(3)	3079(3)	35(1)
C(16)	4445(8)	4828(3)	2815(3)	33(1)
C(17)	4654(8)	4778(3)	2043(3)	32(1)
C(18)	3713(8)	5183(3)	1537(3)	27(1)
C(19)	3965(7)	5103(3)	712(3)	27(1)
C(20)	1405(8)	4055(3)	705(3)	27(1)
C(21)	76(9)	4044(3)	1179(3)	33(2)
C(22)	-329(11)	3467(4)	1549(4)	47(2)
C(23)	580(10)	2909(4)	1445(4)	45(2)
C(24)	1912(10)	2895(4)	973(4)	43(2)
C(25)	2348(9)	3470(3)	609(3)	34(2)
C(26)	2460(8)	4610(3)	-709(3)	29(1)
C(27)	3567(8)	5033(3)	-1068(3)	39(2)

C(28)	3984(8)	4894(4)	-1793(3)	47(2)
C(29)	3346(10)	4349(4)	-2149(4)	50(2)
C(30)	2257(9)	3931(3)	-1802(3)	46(2)
C(31)	1792(8)	4053(3)	-1081(3)	35(1)
C(32)	0(8)	6357(3)	6793(3)	26(1)
C(33)	-1462(8)	6715(3)	6956(3)	30(1)
C(34)	-2400(9)	6533(3)	7557(3)	36(2)
C(35)	-1908(8)	6006(3)	8004(3)	38(2)
C(36)	-450(9)	5640(3)	7830(3)	43(2)
C(37)	450(9)	5814(3)	7224(3)	42(2)
C(38)	2499(8)	5899(3)	5826(3)	26(1)
C(39)	1626(9)	5429(4)	5379(3)	38(2)
C(40)	2364(11)	4815(4)	5287(4)	47(2)
C(41)	3959(10)	4668(4)	5636(4)	43(2)
C(42)	4855(9)	5138(4)	6054(4)	40(2)
C(43)	4132(9)	5759(3)	6155(3)	34(2)
C(44)	2908(7)	7177(3)	6584(3)	32(1)
C(45)	2974(8)	7188(3)	7367(3)	41(1)
C(46)	4065(10)	7631(4)	7775(4)	52(2)
C(47)	5115(9)	8043(3)	7380(4)	56(2)
C(48)	5097(8)	8033(3)	6615(4)	48(2)
C(49)	3985(7)	7604(3)	6208(4)	33(1)
C(50)	3884(8)	7645(3)	5373(4)	40(2)
C(51)	1400(8)	8694(3)	5595(3)	26(1)
C(52)	292(9)	8656(3)	6169(3)	39(2)
C(53)	56(10)	9211(4)	6619(3)	42(2)
C(54)	917(10)	9792(4)	6470(4)	43(2)
C(55)	2021(9)	9813(4)	5903(4)	41(2)
C(56)	2264(9)	9278(3)	5455(3)	32(1)
C(57)	2037(8)	8237(3)	4081(3)	34(1)
C(58)	1084(9)	8777(3)	3775(3)	41(2)
C(59)	1347(10)	8991(4)	3060(4)	52(2)
C(60)	2499(10)	8679(4)	2632(4)	58(2)
C(61)	3429(11)	8163(5)	2916(4)	60(2)
C(62)	3201(9)	7925(3)	3643(4)	45(2)
CI(1)	-2633(2)	6274(1)	120(1)	36(1)

Cl(2)	-1876(2)	4772(1)	-563(1)	32(1)
Cl(3)	-2442(2)	6366(1)	5137(1)	36(1)
Cl(4)	-2173(2)	7936(1)	4493(1)	35(1)
O(1)	3955(5)	7011(2)	4994(2)	43(1)
O(2)	5283(5)	4638(2)	604(2)	34(1)
P(1)	1064(2)	6122(1)	1165(1)	23(1)
P(2)	1886(2)	4813(1)	231(1)	23(1)
P(3)	1344(2)	6643(1)	6057(1)	26(1)
P(4)	1727(2)	7958(1)	5036(1)	27(1)

Table A39 Crystallographic Data for Complex **133**

Empirical formula	$\text{C}_{37.75}\text{H}_{32.50}\text{Cl}_{3.50}\text{NP}_2\text{Pd}$
Formula weight	792.56
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	$a = 11.8852(3)$ Å $\alpha = 113.858(2)^\circ$. $b = 17.3663(5)$ Å $\beta = 95.379(2)^\circ$. $c = 20.1053(8)$ Å $\gamma = 104.5540(10)^\circ$.
Volume	$3582.8(2)$ Å ³
Z	4
Density (calculated)	1.469 Mg/m ³
Absorption coefficient	0.896 mm ⁻¹
F(000)	1606
Crystal size	$0.30 \times 0.18 \times 0.12$ mm ³
Theta range for data collection	1.14 to 33.24° .
Index ranges	$-18 \leq h \leq 18$, $-26 \leq k \leq 26$, $-30 \leq l \leq 30$
Reflections collected	125192
Independent reflections	27390 [$R(\text{int}) = 0.0465$]
Completeness to $\theta = 33.24^\circ$	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9001 and 0.7748
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	27390 / 313 / 1065
Goodness-of-fit on F^2	1.070
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0541$, $wR_2 = 0.1522$
R indices (all data)	$R_1 = 0.0859$, $wR_2 = 0.1790$
Largest diff. peak and hole	3.364 and -1.528 e.Å ⁻³

Table A40 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex **133**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
C(14)	8481(10)	2664(9)	6861(10)	26(3)
C(15)	8545(15)	1824(10)	6650(10)	48(3)
C(16)	9501(17)	1582(12)	6321(12)	62(3)
C(17)	10349(16)	2181(15)	6221(14)	66(5)
C(18)	10300(20)	3039(15)	6460(17)	71(7)
C(19)	9322(14)	3286(8)	6749(10)	36(3)
C(14A)	8508(18)	2662(14)	6903(16)	46(5)
C(15A)	8844(17)	1944(12)	6830(11)	41(3)
C(16A)	9878(19)	1851(16)	6547(13)	58(4)
C(17A)	10537(19)	2452(17)	6354(15)	59(5)
C(18A)	10140(20)	3152(15)	6383(16)	46(4)
C(19A)	9100(20)	3250(14)	6658(16)	47(4)
C(38)	5180(20)	8087(14)	8702(14)	35(5)
C(39)	4980(20)	8901(12)	9005(12)	61(5)
C(40)	4160(30)	9018(12)	9459(14)	79(6)
C(41)	3620(30)	8364(15)	9639(16)	69(6)
C(42)	3764(19)	7536(10)	9312(10)	41(5)
C(43)	4580(30)	7402(17)	8850(20)	30(4)
C(38A)	5114(17)	8125(12)	8642(13)	35(5)
C(39A)	4630(20)	8803(13)	8773(17)	55(5)
C(40A)	3740(30)	8875(16)	9170(20)	81(7)
C(41A)	3310(20)	8262(14)	9422(17)	66(6)
C(42A)	3840(20)	7618(16)	9326(14)	75(9)
C(43A)	4740(30)	7525(17)	8931(19)	38(6)
Pd(1)	5646(1)	4064(1)	8042(1)	24(1)
Pd(2)	6420(1)	8857(1)	7531(1)	28(1)
C(1)	4508(3)	1851(2)	6629(2)	29(1)
C(2)	4998(4)	1575(3)	6007(2)	43(1)
C(3)	4263(5)	969(3)	5307(2)	56(1)
C(4)	3056(4)	667(3)	5234(3)	56(1)

C(5)	2567(4)	935(3)	5851(3)	50(1)
C(6)	3278(3)	1526(3)	6547(2)	39(1)
C(7)	4794(3)	2133(2)	8148(2)	27(1)
C(8)	4734(4)	1274(2)	8010(2)	42(1)
C(9)	4283(5)	935(3)	8483(3)	52(1)
C(10)	3896(5)	1449(3)	9084(2)	52(1)
C(11)	3930(4)	2288(3)	9208(2)	45(1)
C(12)	4390(3)	2643(2)	8748(2)	32(1)
C(13)	6882(3)	2414(2)	7543(2)	27(1)
C(20)	7531(3)	2674(2)	8324(2)	25(1)
C(21)	7823(3)	2024(2)	8468(2)	35(1)
C(22)	8371(4)	2205(2)	9180(2)	42(1)
C(23)	8652(3)	3047(2)	9756(2)	34(1)
C(24)	8371(3)	3703(2)	9621(2)	29(1)
C(25)	7813(3)	3537(2)	8914(2)	24(1)
C(26)	8685(3)	4952(2)	8496(2)	29(1)
C(27)	9746(3)	4767(2)	8552(2)	31(1)
C(28)	10712(3)	5199(3)	8343(2)	39(1)
C(29)	10605(4)	5806(3)	8087(2)	45(1)
C(30)	9533(4)	5972(3)	8016(3)	53(1)
C(31)	8579(4)	5558(3)	8227(3)	46(1)
C(32)	7514(3)	5205(2)	9743(2)	28(1)
C(33)	6727(3)	4951(2)	10141(2)	34(1)
C(34)	6855(4)	5493(3)	10894(2)	41(1)
C(35)	7765(4)	6299(3)	11245(2)	46(1)
C(36)	8520(4)	6573(3)	10850(2)	48(1)
C(37)	8403(3)	6026(2)	10098(2)	38(1)
C(44)	7711(14)	8290(20)	8760(13)	36(8)
C(45)	7840(30)	8118(17)	9372(13)	60(6)
C(46)	8890(20)	8300(20)	9864(17)	67(10)
C(47)	9910(20)	8685(17)	9685(13)	60(6)
C(48)	9871(14)	8910(20)	9095(14)	67(6)
C(49)	8787(14)	8704(19)	8641(15)	62(6)
C(44A)	7517(15)	8250(20)	8891(12)	23(3)
C(45A)	8201(10)	7700(7)	8790(7)	35(3)
C(46A)	9110(19)	7870(12)	9366(11)	54(5)

C(47A)	9333(17)	8596(13)	10057(15)	64(7)
C(48A)	8577(12)	9157(9)	10177(7)	45(3)
C(49A)	7693(9)	8972(7)	9593(5)	30(2)
C(44B)	7735(12)	8092(15)	8625(11)	33(4)
C(45B)	7710(20)	7906(13)	9248(11)	41(4)
C(46B)	8865(17)	8060(20)	9650(15)	56(6)
C(47B)	9920(20)	8310(20)	9426(15)	76(8)
C(48B)	9916(13)	8449(17)	8785(13)	61(5)
C(49B)	8801(12)	8298(16)	8377(13)	57(5)
C(50)	5906(3)	6821(2)	7487(2)	31(1)
C(51)	7024(4)	5956(3)	6660(2)	45(1)
C(52)	6519(5)	5191(3)	6726(2)	51(1)
C(53)	6840(6)	4432(4)	6349(3)	73(2)
C(54)	7675(7)	4456(5)	5910(3)	88(2)
C(55)	8139(6)	5202(6)	5832(4)	84(2)
C(56)	7831(5)	5945(5)	6192(3)	67(2)
C(57)	4620(3)	6462(2)	7070(2)	28(1)
C(58)	3858(3)	5772(2)	7151(2)	34(1)
C(59)	2654(4)	5433(2)	6807(2)	39(1)
C(60)	2204(4)	5773(3)	6375(2)	44(1)
C(61)	2953(3)	6461(3)	6281(2)	40(1)
C(62)	4168(3)	6812(2)	6623(2)	27(1)
C(63)	5802(3)	7245(2)	5745(2)	31(1)
C(64)	5408(4)	6352(3)	5271(2)	47(1)
C(65)	5974(5)	6001(3)	4706(2)	53(1)
C(66)	6912(5)	6539(3)	4594(2)	54(1)
C(67)	7330(7)	7424(4)	5067(4)	90(2)
C(68)	6774(6)	7784(3)	5645(3)	72(2)
C(69)	4045(3)	8157(2)	6169(2)	31(1)
C(70)	3666(4)	7911(3)	5420(2)	40(1)
C(71)	2811(5)	8216(4)	5184(3)	56(1)
C(72)	2340(6)	8761(4)	5691(3)	70(2)
C(73)	2705(6)	9022(4)	6441(3)	76(2)
C(74)	3568(5)	8727(3)	6678(2)	56(1)
C(75)	259(8)	9827(10)	2663(6)	172(6)
C(76)	9790(20)	2696(12)	4096(11)	189(11)

CI(1)	3815(1)	3731(1)	7282(1)	35(1)
CI(2)	5816(1)	5591(1)	8636(1)	36(1)
CI(3)	7848(4)	9991(2)	8561(2)	63(1)
CI(3A)	7385(6)	10096(3)	8688(3)	42(1)
CI(4)	6567(1)	9779(1)	6915(1)	34(1)
CI(5)	260(2)	10441(2)	3592(2)	155(1)
CI(6)	-1104(2)	9083(2)	2144(2)	140(1)
CI(7)	9881(7)	3637(5)	4809(5)	176(3)
CI(8)	9519(9)	2366(7)	3154(9)	279(6)
N(1)	7494(3)	2852(2)	7141(2)	31(1)
N(2)	6798(3)	6747(2)	7045(2)	38(1)
P(1)	5422(1)	2607(1)	7558(1)	24(1)
P(2)	7425(1)	4428(1)	8793(1)	24(1)
P(3)	6300(1)	8014(1)	8137(1)	29(1)
P(4)	5105(1)	7740(1)	6507(1)	25(1)

Table A41 Crystallographic Data for Complex (*R*)-**138**

Empirical formula	$\text{C}_{40}\text{H}_{38}\text{ClNO}_5\text{P}_2\text{Pd}$	
Formula weight	816.50	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	$a = 11.1540(4)$ Å	$\alpha = 90^\circ$.
	$b = 16.6940(7)$ Å	$\beta = 90^\circ$.
	$c = 21.0834(7)$ Å	$\gamma = 90^\circ$.
Volume	$3925.8(3)$ Å ³	
Z	4	
Density (calculated)	1.381 Mg/m ³	
Absorption coefficient	0.665 mm ⁻¹	
F(000)	1672	
Crystal size	0.30 x 0.24 x 0.20 mm ³	
Theta range for data collection	2.20 to 26.71°.	
Index ranges	-14 ≤ h ≤ 14, -13 ≤ k ≤ 21, -	
	26 ≤ l ≤ 26	
Reflections collected	41122	
Independent reflections	8275 [R(int) = 0.0385]	
Completeness to theta = 26.71°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8785 and 0.8255	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8275 / 102 / 500	
Goodness-of-fit on F ²	1.103	
Final R indices [I > 2σ(I)]	R ₁ = 0.0274, wR ₂ = 0.0623	
R indices (all data)	R ₁ = 0.0356, wR ₂ = 0.0768	
Absolute structure parameter	-0.02(2)	
Largest diff. peak and hole	0.375 and -0.206 e.Å ⁻³	

Table A42 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex (*R*)-**138**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
C(1)	1985(3)	3168(2)	7932(1)	34(1)
C(2)	2442(3)	3039(2)	7314(2)	41(1)
C(3)	3277(3)	3549(2)	7057(2)	44(1)
C(4)	3711(3)	4213(2)	7390(2)	37(1)
C(5)	4605(3)	4718(2)	7135(2)	44(1)
C(6)	5033(3)	5344(2)	7470(2)	53(1)
C(7)	4588(3)	5508(2)	8082(2)	50(1)
C(8)	3724(3)	5035(2)	8341(2)	40(1)
C(9)	3257(3)	4363(2)	8013(2)	34(1)
C(10)	2399(3)	3823(2)	8273(1)	32(1)
C(11)	1901(3)	3932(2)	8938(2)	31(1)
C(12)	776(3)	4453(2)	8926(2)	42(1)
C(13)	2834(3)	2719(2)	9350(2)	39(1)
C(14)	918(3)	3114(2)	9769(1)	37(1)
C(15)	-1598(3)	458(2)	9246(2)	35(1)
C(16)	-643(4)	56(2)	9537(2)	55(1)
C(17)	-885(5)	-628(3)	9871(2)	72(1)
C(18)	-2061(5)	-915(2)	9919(2)	69(1)
C(19)	-2986(4)	-516(2)	9638(2)	54(1)
C(20)	-2759(3)	179(2)	9301(2)	40(1)
C(21)	-2438(3)	2010(2)	8701(2)	31(1)
C(22)	-2364(3)	2757(2)	8991(2)	35(1)
C(23)	-3260(3)	3318(2)	8906(2)	48(1)
C(24)	-4217(4)	3138(2)	8521(2)	56(1)
C(25)	-4299(3)	2403(3)	8234(2)	61(1)
C(26)	-3413(3)	1831(2)	8320(2)	49(1)
C(27)	-794(3)	1003(2)	8010(1)	32(1)
C(28)	-929(3)	267(2)	7802(2)	40(1)
C(29)	881(3)	1298(2)	7000(1)	33(1)

C(30)	1708(3)	717(2)	7178(2)	40(1)
C(31)	2338(3)	312(2)	6721(2)	49(1)
C(32)	2184(4)	489(2)	6090(2)	54(1)
C(33)	1390(4)	1061(2)	5912(2)	52(1)
C(34)	718(3)	1474(2)	6360(2)	43(1)
C(35)	-1093(3)	2389(2)	7196(1)	35(1)
C(36)	-2026(3)	2013(2)	6879(2)	50(1)
C(37)	-2849(3)	2461(3)	6538(2)	62(1)
C(38)	-2737(4)	3290(3)	6508(2)	71(1)
C(39)	-1802(5)	3664(3)	6813(2)	79(2)
C(40)	-988(4)	3222(2)	7166(2)	60(1)
N(1)	1670(2)	3102(1)	9187(1)	30(1)
O(1)	-131(2)	1747(1)	9078(1)	32(1)
Cl(1)	3392(7)	455(4)	9297(3)	37(1)
O(2)	3865(9)	-334(5)	9434(6)	62(3)
O(3)	2544(11)	386(7)	8802(6)	94(4)
O(4)	4310(4)	975(3)	9122(3)	67(2)
O(5)	2761(9)	754(6)	9834(4)	88(4)
Cl(1A)	3229(8)	297(5)	9382(4)	45(2)
O(2A)	4243(9)	-190(7)	9355(7)	69(4)
O(3A)	2958(13)	610(8)	8780(4)	88(4)
O(4A)	2271(6)	-220(5)	9550(4)	87(3)
O(5A)	3352(10)	848(6)	9875(5)	76(4)
P(1)	-1204(1)	1332(1)	8795(1)	29(1)
P(2)	33(1)	1813(1)	7613(1)	30(1)
Pd(1)	913(1)	2456(1)	8428(1)	29(1)