Syntheses of bifunctionalized phosphine complexes via ruthenium promoted stepwise hydrophosphination, insertion, hydration, and hydroamination reactions

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**SYNTHESES OF BIFUNCTIONALIZED PHOSPHINE
COMPLEXES VIA RUTHENIUM PROMOTED STEPWISE
HYDROPHOSPHINATION, INSERTION, HYDRATION,
AND HYDROAMINATION REACTIONS**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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Abbreviations and Symbols

acac	acetylacetonate
Anal.	analytical
Ar	aryl group
ax	axial
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
br.	broad
BOC	t-butoxycarbonyl
bp.	boiling point
<i>c</i>	sample concentration for O.R.D analysis
ca.	about (Latin <i>circa</i>)
cat	catalyst
clacd.	calculated
CDCl ₃	chloroform-d ₁
CD ₂ Cl ₂	dichloromethane-d ₂
CHIRAPHOS	2,3-bis(diphenylphosphino)butane
COD	1,5-cyclooctadiene
conc.	concentrated
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadiene

d	day(s) (for reaction time)
d	doublet (in NMR assignments)
dcpe	1,2-bis(dicyclohexylphosphino)ethane
dd	doublet of doublets (in NMR assignments)
dt	doublet of triplets (in NMR assignments)
ddq	doublet of doublet of quartets (in NMR assignments)
dec.	decomposition
DIOP	2,3- <i>O</i> -isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino) butane
DIPAMP	1,2-bis[(<i>o</i> -methoxyphenyl)phenylphosphino]ethane
dm	decimeter
DMPP	3,4-dimethyl-1-phenylphosphole
DOPA	dihydroxyphenylalanine
DPEphos	bis(2-diphenylphosphino)phenyl ether
dppe	1,2-bis(diphenylphosphino)ethane
dppf	1,1'-bis(diphenylphosphino)ferrocene
dppm	bis-(diphenylphosphino)methane
e	electron
EDTA	ethylenediaminetetraacetic acid
e.e.	enantiomeric excess
e.g.	for example
eq.	equatorial

eq.	equivalent
ES	electrospray
Et	ethyl
g	gram(s)
h	hour(s)
HCl	hydrochloric acid
hmpa	hexamethylphosphoramide
HPAs	heteropoly acids
Hz	hertz
i.e.	that is (Latin <i>id est</i>)
IR	infrared
L	generalized ligand
m	multiplet (in NMR assignments)
M	metal type
Me	methyl
MDPP	methyldiphenylphosphine
mg	milligrams
MHz	megahertz
min	minutes
mL	mililiter
m.p.	melting point
NMDPP	neomethyldiphenylphosphine

NMR	Nuclear Magnetic Resonance
NOE	Nuclear Overhauser Effect
<i>o</i>	<i>ortho</i>
O.R.D.	Optical Rotation Dispersion
Ph	phenyl
ppm	parts per million
q	quartet (in NMR assignments)
<i>R</i>	rectus (Latin: absolute configuration)
ROESY	2D rotating frame Nuclear Overhauser Enhancement
<i>S</i>	sinister (Latin: absolute configuration)
s	singlet (in NMR assignments)
solv	solvent
T	temperature
tcep	tris(cyanoethyl)phosphine
THF	tetrahydrofuran
TMS	trimethylsilyl
X	generalized ligand
Xantphos	9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene
°	degree (for angles)
Å	angstrom(s)
°C	degree celsius
$^nJ_{AB}$	n-bond coupling constant between nuclei A and B

σ	sigma bonding
η	hapticity in π -bonding ligands
μ	descriptor for bridging
δ	NMR chemical shift in ppm (in NMR assignments)
δ^-	partial negative charge
δ^+	partial positive charge
$[\alpha]_D$	specific rotation measured at sodium D line (589nm)

List of Compounds Synthesized

Summary

This thesis describes the asymmetric syntheses of bifunctionalized phosphine complexes, which contain a stereogenic center at phosphorus, through various reactions, including insertion, hydrophosphination, hydration, and hydroamination. Promoted by the coordination of diprop-1-ynylphenylphosphine to ruthenium, the two alkyne moieties thereafter were functionalized by different reactions, which thus led to the formation of a chiral phosphorous center. This strategy presented is valuable and can be widely used in the synthesis of chiral phosphines.

Activated by the coordination of prochiral diprop-1-ynylphenylphosphine to ruthenium, one of the two alkyne moieties then underwent hydrophosphination with diphenylphosphine. This process stereoselectively generated a diphosphine complex bearing a stereogenic center at one phosphorous atom. The remaining unreacted alkynyl group subsequently inserted into the Pd-C bond of an organopalladium complex to give an unique heterobimetallic ruthenium(II)-palladium(II) complex that contained a chiral and bifunctionalized phosphine. The structure of the bimetallic product also contains a tridentate ligand chelating to palladium, which is proposed to be generated through a proton exchange process aided by palladium. Furthermore, this bimetallic complex exists as two interconvertable conformations in a ratio of 3:1 in dichloromethane or chloroform. The corresponding structures and the equilibrium between them were studied and described.

The coordination of alkynylphenylphosphine to ruthenium also promotes the insertion of the alkyne moiety into the Pd-C bond of cyclopalladated complexes involving benzylamines to generate heterobimetallic ruthenium(II)-palladium(II) complexes with high reactivity. It is noteworthy that if the organopalladium dimer is chiral, this insertion process can induce a stable stereogenic center at ruthenium stereoselectively. Furthermore, for diprop-1-ynylphenylphosphine in the reactant, conversion of one of the two alkynyl groups into a carbon-carbon double bond introduces a chiral center at phosphorus. Therefore, the reaction of the diprop-1-ynylphenylphosphine ruthenium complex and the nonchiral cyclopalladated complex gave two diastereomerically related pairs of enantiomers, which could then interconvert between themselves at room temperature in solution. On the other hand, the reaction of the diprop-1-ynylphenylphosphine ruthenium complex and the chiral cyclopalladated complex gave two stable diastereoisomers bearing two stereogenic centers at ruthenium and phosphorus. It is noteworthy that the products resulting from the dialkynylphosphine complex contain an unreacted alkyne moiety which can be further functionalized.

For the insertion products resulting from the dialkynylphosphine complexes, the remaining unreacted alkynyl group can be converted into the ketonyl group by hydration and thus gave a bifunctionalized phosphine complex. It is noteworthy that the absolute configuration at phosphorus remained unchanged after the hydration. The reaction conditions have been optimized and moderate yields were obtained by using a mixed solvent of dichloromethane, acetone, and water in the 2:10:1 ratio. An unusual Pd-C-P-C

4-membered ring, which adopts a slightly distorted planar geometry, is observed in the structures of the hydration products. These structures were identified by single crystal X-ray diffraction experiments. Moreover, the hydration products are bimetallic zwitterions with both anionic palladium(II) and cationic ruthenium(II).

Apart from hydration, the insertion products resulting from the dialkynylphosphine complexes can also undergo the hydroamination reaction under mild condition to convert the remaining unreacted alkyne moiety to an imino group. The absolute configuration at phosphorus in the resulting bifunctionalized phosphine complexes was retained after this process. A variety of amines can be used for this hydroamination reaction. Similar to the hydration product, an unusual Pd-C-P-C 4-membered ring, which adopts a slightly distorted planar geometry, is generated in the hydroamination products. Furthermore, the hydroamination products are bimetallic zwitterions with an anionic palladium(II). The positive charge is found to be located at the protonized nitrogen of the imine moiety.

Chapter 1

General Introduction

1.1 Insertion Reactions

Insertion is an important reaction because it is generally regarded as a key step in homogenous catalysis and stoichiometric organometallic syntheses. An insertion reaction involves the formal insertion of one ligand (usually unsaturated) into another metal-ligand bond on the same complex as shown in Scheme 1-1.

Scheme 1-1

The two main types of insertions are 1,1- and 1,2-insertion, which are shown in Scheme 1-2.¹ In the 1,1-insertion product, both bonds to the inserted molecule are made to the same atom in that molecule. For example, both M and the X group are bonded to the carbon of the inserted CO. However, in 1,2-insertion product, bonds to the inserted molecule are made to adjacent atoms in that molecule. For example, M is bonded to one carbon, and the X group is bonded to the neighboring carbon in the reaction involving an inserted olefin. The insertion type observed in any given case depends on the nature of

the 2e inserting ligand. In general, η^1 ligands tend to undergo 1,1-insertion, and η^2 tend to undergo 1,2-insertion. For instance, CO gives only the 1,1-insertion products, while an olefin gives the 1,2-insertion products. It is noteworthy that SO₂ is the only common ligand that can give both types of insertion, i.e., η^1 (S) and η^2 (S, O).¹

1,1-insertion

1,2-insertion

Scheme 1-2 (the square indicates the vacant coordination site)

Both the 1,1- and 1,2-insertion reactions show the following general features. Firstly, both insertion processes generate a vacant coordination site, which can be occupied by the external ligands and the insertion product can then be trapped. Secondly, both insertion reactions require a *cis* arrangement of the reacting ligands. Thirdly, the formal oxidation state of the metal center remains unchanged during the reaction.

In principle, insertion reactions are reversible. However, only one of the two possible directions is strongly thermodynamically preferred in many cases. For example, in the insertion of SO₂ into the M–R bond, the generation of an alkyl sulfinate complex, rather than the elimination of it to generate SO₂, is normally observed. In contrast,

diazoarene complexes readily eliminate N₂, while the reverse insertion of N₂ into a metal–aryl bond has not yet been reported.¹

1.1.1 Carbonyl Insertion

Carbonyl insertion is one of the most well-studied insertion reactions. It involves the reaction of CO with an alkyl complex to give an acyl (-COR) product.² The best-known example is the reaction of CH₃Mn(CO)₅ with CO, as shown in Scheme 1-3.

Scheme 1-3

The mechanism of migratory insertion shown in Scheme 1-4 has been applied in many cases. The alkyl group in the reagent undergoes a migration to the CO, rather than the migration of CO, to give an acyl intermediate, which is subsequently trapped by the added ligand, L, to generate the final product.³⁻⁶ Furthermore, any stereochemistry present at the alkyl carbon is retained in the insertion.⁶⁻⁸

Scheme 1-4 (the square indicates the vacant coordination site)

Hydroformylation reaction

Monsanto acetic acid synthesis

Reppe synthesis

Scheme 1-5

Carbonyl insertion is one of the most fundamental reactions in organometallic chemistry. A large number of examples of CO insertion reactions have been reported in the past few decades.⁹⁻¹⁹ Apart from Mn complexes, CO insertion reactions have also been observed with complexes bearing other metals, such as Zr,^{20, 21} V,²² Cr,^{23, 24} Mo,²⁵ Fe,^{26, 27} Ru,^{28, 29} Co,³⁰ Rh,³¹ Ni,^{30, 32} Pd,^{33, 34} Pt,³⁵⁻³⁷ and Cu.^{38, 39} Many important organic compounds can be synthesized through catalytic reactions involving this process.^{40, 41} Significant examples (Scheme 1-5) include the well-known hydroformylation reaction, which converts olefins to aldehydes or alcohols,^{42, 43} the Monsanto acetic acid synthesis, which converts methanol to acetic acid,^{44, 45} and the Reppe synthesis affording acids (or esters) from olefins.³⁹

1.1.2 Insertions Involving Alkenes

The insertion of coordinated alkene ligands into M-H bonds is an important reaction due to its potential for the formation of alkyl derivatives. Furthermore, this process also constitutes a key step in various catalytic reactions including alkene polymerization, which is possibly the most commercially important organometallic reaction.¹ Alkenes undergo the 1,2-insertion due to the nature of η^2 -ligands. In some insertion reactions, agostic alkyl intermediates, rather than classical ones, were generated (Scheme 1-6).⁴⁶ Not only the thermodynamics of the particular system, but also the nature of the alkene involved, strongly affects the equilibrium position. For example, for ethylene,⁴⁷ the equilibrium tends to move to the left (i.e., the alkyl β -eliminates). In contrast, for alkenes with electron-withdrawing substituents (e.g., C_2F_4), the equilibrium lies entirely to the right since the resulting alkyls such as $L_nMCF_2CF_2H$ with electron-withdrawing substituents have very strong M-C bonds, preventing the elimination involving the β hydrogen (Scheme 1-7).

Scheme 1-6

Scheme 1-7

In the insertion mode of Pd-H addition to an unsymmetrical *cis* alkene, the Pd-H hydride acts as a hydridic δ^- group (Scheme 1-8), which determines the regiochemistry of this reaction.⁴⁸ Hydrozirconation of alkenes by Cp_2ZrHCl is another example related to regiochemistry of an alkene insertion. Terminal alkenes insert in an *anti*-Markovnikov manner to give a stable primary alkyl rather than an unstable secondary alkyl (Scheme 1-9). The insertion proceeds in this way since the primary alkyl is thermodynamically more stable than any secondary alkyl, possibly due to steric reasons.⁴⁹ The usual stereochemistry of the insertion is *syn*, because the transition state involves an essentially coplanar M-C-C-H arrangement, which implies that both insertion and elimination processes require the M-C-C-H system to be capable of adopting coplanar (Scheme 1-10). The *cis* compound undergoes the insertion into the coordinated cycloocta-1,5-diene at least 40 times more rapidly than the *trans* compound, since the *cis* compound rather than the *trans* one is possible to form a coplanar M-C-C-H arrangement, although the alkene and M-H groups are *cis* in both cases.⁵⁰

Scheme 1-8

Scheme 1-9

Scheme 1-10

Alkene insertion takes place into the M-H bond more commonly than the M-R bond since reactions involving M-H are almost always kinetically more facile than reactions involving M-R.⁵¹ However, there are still some examples of insertion into M-R, such as the insertion of ethylene into an Co-C bond that was evidenced by the labeling experiment, as shown in Scheme 1-11.⁵² Moreover, alkene polymerization that involves repeated alkene insertion into the M-R bonds is another important example of the insertion into the M-R bond (Scheme 1-12).²

Apart from the 1,2-insertion reactions with a variety of hydrides, butadiene also reacts with HMn(CO)_5 through the 1,4-insertion pathway. The mechanism is described to be a H atom transfer to give a 1,1-dimethylallyl radical, which is subsequently trapped by the metal (Scheme 1-13).⁵³ Therefore only substrates that can form especially stable radicals are able to undergo this 1,4-insertion reaction (e.g., 1,3-diene $\rightarrow$ allyl radical).

Scheme 1-11

Scheme 1-12

Scheme 1-13

Two main applications of alkene insertion include metal-catalyzed organic synthesis and alkene polymerization. An important example of the application in organic chemistry is hydrogenation, one of the most important reactions known and widely used in organic synthesis. In the presence of homogeneous catalysts, the hydrogenation process of olefin normally includes an insertion into the M-H bond. Illustrative homogeneous catalysts include the rhodium-based compound known as Wilkinson's catalyst⁵⁴⁻⁵⁸ and the iridium-based Crabtree's catalyst (Scheme 1-14).^{50, 58-61}

Scheme 1-14

Another important example of an organic reaction involving an insertion in the mechanism is the Heck reaction. Through the Heck reaction, an unsaturated halide (or triflate) reacts with an alkene in the presence of a strong base and an organopalladium catalyst to give a substituted alkene (Scheme 1-15).⁶²⁻⁶⁶ The halide or triflate can be an aryl, benzyl, or vinyl compound. The alkene involved, such as acrylate ester or an acrylonitrile, is often electron-deficient and contains at least one proton. Tetrakis(triphenylphosphine)palladium(0), palladium chloride, or palladium(II) acetate are the potential catalysts for the Heck reaction. Triphenylphosphine and BINAP have been applied as the supporting ligands. The reaction often involves external bases such as triethylamine, potassium carbonate, and sodium acetate. Investigations of the reaction mechanism indicate that an insertion of olefin into a Pd-C bond is included in this process.⁶³ Beside the Heck reaction, many other catalytic organic reactions such as dimerization⁶⁷ and oligomerization⁶⁸ of olefins also involve the insertion of alkenes.

Scheme 1-15

The other important application of insertion of alkene is polymerization reactions such as the well-known Ziegler-Natta catalysis process. A Ziegler-Natta catalyst is a reagent or a mixture of reagents typically based on titanium or organometallic aluminium compounds. For example, triethylaluminium $[(C_2H_5)_3Al]$, has been applied in the polymerization of terminal 1-alkenes(α -olefins).⁶⁹⁻⁷¹ According to Cossee-Arlman mechanism,^{72, 73} a polymer chain can grow as a consequence of repeated 1,2-insertions of olefins. Several important polymers such as polypropylene, amorphous poly-alpha-olefins (APAO), polyvinyl alcohol, and polyacetylene have been produced in the presence of Ziegler-Natta catalysts.

1.1.3 Other Insertion Reactions

Insertions of sulfur dioxide have also been reported. Sulfur dioxide is a strong electrophilic species, which has a vacant orbital on the S atom, therefore it is able to attack even 18e metal complexes. The electrophilic attack can take place at the α carbon of the alkyl group from the side opposite to the metal to give an alkyl sulfinate ion (RSO_2^-) with inversion of the configuration at the carbon.⁷⁴⁻⁷⁶ Since the oxygen atoms have higher density of the negative charge, the kinetic product of ion recombination is the O-bound sulfinato complex. On the other hand, the S-bound sulfinate forms normally as a thermodynamic product when a softer metal is involved in this process (since S is softer than O). This sequence constitutes a 1,2- (if the sulfinate is O bound in the product) or a 1,1-insertion of SO_2 (if S bound). A notable feature of this mechanism is that the SO_2 does not need to bind to the metal before insertion, so a 2e vacant site on the active metal

center is not necessary, which indicates the possibility of the reaction between SO₂ and the 18e complexes (Scheme 1-16).

Scheme 1-16

Scheme 1-17

In term of the insertion reaction mechanism, isocyanides behave in a similar manner to CO. Isocyanides insert very readily into a M-R bond and even a M-H bond to give iminoacyls, which are usually η^2 bound for the early metals⁷⁷ or in metal clusters.⁷⁸ Additionally, substrates containing other metals such palladium^{79, 80} and platinum⁸¹ have also been reported in insertion reactions involving isocyanides (Scheme 1-17).

In recent decades many examples of insertions of CO₂ into M-E (E=C, H, N, O, P, Si or other metal) bonds have been reported. Carbon dioxide is thermodynamically highly stable and kinetically inert. However, coordination of CO₂ to a transition metal center lowers the activation energy required in further reactions, thus it is possible to convert this relatively inert molecule with suitable reactants into useful products.⁸² There are two possible products obtained from insertion of CO₂ into a M-E bond in different ways, as shown Scheme 1-18. For insertion reactions involving M-H⁸³⁻⁸⁶ and M-C⁸⁷⁻⁹¹ bonds, route A occurred more frequently.

Scheme 1-18

Additionally, a rare example of O₂ insertion into a M-X bond, which involves Pt(IV)-H, has also been reported⁹², as shown in Scheme 1-19.

Scheme 1-19

1.2 Metal-Catalyzed Hydrophosphination

In term of synthetic value and atom economy, the addition of P-H bonds to unsaturated compounds is an important reaction in organophosphorus chemistry.^{93, 94} Reactions involving P(III) reagents are named hydrophosphination, while reactions involving P(V) reagents are named hydrophosphinylation (secondary phosphine oxides as reactants) or hydrophosphorylation (hydrogen phosphonates as reactants) (Scheme 1-20).⁹⁵

Scheme 1-20

The main substrates of hydrophosphination reactions include alkenes, alkynes, and carbonyl compounds. This process proceeded by thermal,⁹⁶⁻⁹⁸ acidic,^{99, 100} basic,¹⁰¹⁻¹⁰⁴ or free radical¹⁰⁵⁻¹¹⁰ pathways. However, the use of transition metal complexes for such reactions often offers vast improvement in rate, selectivity, and stereocontrol. Several transition metal complexes such as Ni,¹¹¹⁻¹¹³ Pd,¹¹³ Pt,¹¹⁴⁻¹¹⁷ Co,¹¹⁸ Ru,¹¹⁹ and Ln¹²⁰⁻¹²⁶ complexes have already been applied to catalyze hydrophosphination reactions. Moreover, many functional groups can be incorporated into the substrates without special protection since the reaction conditions required are usually relatively mild. Apart from catalytic processes, there are examples of hydrophosphination reactions, which are promoted by stoichiometric quantities of transition metal complexes,¹²⁷⁻¹³⁷ including synthesis of chiral phosphines via metal complex promoted asymmetric addition of P-H moiety across carbon-carbon unsaturated compounds.^{136, 137}

1.2.1 Transition Metal-Catalyzed Hydrophosphination of Alkene

Michael-type activated substrates such as acrylonitrile or ethyl acrylate usually serve as the substrates of hydrophosphination reactions in the presence of various metal complexes.

The reaction of acrylonitrile ($\text{CH}_2=\text{CHCN}$) with PH_3 or $\text{PH}(\text{CH}_2\text{CH}_2\text{CN})_2$, which was catalyzed by tris(cyanoethyl)phosphine complex $[\text{Pt}\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3\}_3]$, generated $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$, as shown in Scheme 1-21.¹³⁸ When monitored using the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, the product could not be observed after 6-8 h if the phosphine and

acrylonitrile were alone present. However, the reaction was completed upon the addition of the catalyst $\text{Pt}(\text{tcep})_3$. Although other d^8 and d^{10} metal-tcep complexes, such as Pd, Ir, and Ni complexes, are also found to be potential catalysts for this hydrophosphination reaction, with the $\text{Pt}(0)$ catalyst being the most efficient.¹¹⁶

Kinetic studies proposed the possible mechanisms. Scheme 1-22 shows the process at high concentration of $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$. This process, which is called the mononuclear mechanism, involves the P-H oxidative addition and the P-C reductive elimination. However, if a low concentration of $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$ was used, the hydrophosphination process proceeded through a different pathway, named as binuclear mechanism.¹¹⁶ It is noteworthy that the phosphines formed did not suppress the hydrophosphination reaction, in spite of that the excess phosphines were often inhibitory in many other catalytic reactions. In agreement with this, the resulting phosphine $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$ was reluctant to form tetrakis(phosphine)platinum species, allowing the metal complex to be coordinatively unsaturated. Likewise, the bis(phosphine)(acrylonitrile)platinum complex did not undergo the displacement of the acrylonitrile ligand with $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$ even in the presence of 50 equiv of the phosphine. Furthermore, the binuclear μ -phosphido complex in Scheme 1-22 was regarded as a possible intermediate, since it was also a catalyst precursor for hydrophosphination of acrylonitrile.

Scheme 1-21

Scheme 1-22

The steps of the insertion of the alkene and the subsequent elimination include two possible pathways. Firstly, oxidative addition of the P-H bond, a P-C bond forms through the P-C reductive elimination following the insertion of the unsaturated substrate into the M-H bond, or through the C-H reductive elimination following the insertion into the M-P bond. Detailed mechanistic studies revealed that the Pt-catalyzed acrylonitrile hydrophosphination followed the latter mechanism. (Scheme 1-23).¹³⁹

Scheme 1-23

Like acrylonitrile, the reactivity of hydrophosphination of ethyl acrylate is also very facile. In the presence of 0.002 equiv of Pt(0) catalyst, PH_3 reacted with ethyl acrylate smoothly to give $\text{P}(\text{CH}_2\text{CH}_2\text{COOEt})_3$ and the telomer within 8 h (Scheme 1-24). The selectivity for $\text{P}(\text{CH}_2\text{CH}_2\text{COOEt})_3$ was higher than 90% . Compared with the radical process, the metal-catalyzed method was much cleaner.¹⁴⁰

Scheme 1-24

Styrene hydrophosphination with HPPH_2 has also been reported. Catalyzed by $\text{Ni}[\text{P}(\text{OEt})_3]_4$ and Et_3N , this reaction proceeded with high yield and selectivity. Furthermore, the hydrophosphination reactions of styrene and several substituted styrenes were observed to only give the *anti*-Markovnikov products.¹¹³

In contrast, the reaction of $\text{CH}_2=\text{CHCF}_3$ with PH_3 in the presence of Pt(0) catalysis was found to be totally unreactive, which indicated that the resonance (or Michael) activation of alkene was critical for this hydrophosphination process.¹⁴⁰

Asymmetric hydrophosphination catalyzed by a chiral phosphine Pt complex gave P-chiral and C-chiral products (Scheme 1-25), although the ee value was not high.^{117, 141}

For example, the reaction of methacrylonitrile and the bulky secondary phosphines were catalyzed by $[\text{CpFeC}_5\text{H}_3(\text{PPh}_2)(\text{CHMe})]_2\text{CyP-Ni}(\text{THF})\text{X}_2$ ($\text{X} = \text{ClO}_4$, BPh_4 or BF_4) to give high yields and ee values of 45-89%. Crystallographic data for the CH_2CMeCN adduct of the Ni catalyst revealed that the two axial faces of the complex were differentiated by the displacement of the $\text{Ni}(\text{CH}_2\text{CMeCN})$ from the three P atoms in the ligand, accounting for the stereoselectivity.^{111, 112}

Scheme 1-25

1.2.2 Transition Metal-Catalyzed Hydrophosphination of Alkyne

It has been well established that alkenylphosphines including functionalized derivatives are useful ligands for the activation of various coordinated substrates and as precursors of a variety of functional ligands by modification of the $\text{C}=\text{C}$ bond for organic synthesis, including enantioselective catalysis. However, standard syntheses of vinylphosphines are unsatisfactory due to either limited substrates or poor stereoselectivity. Transition metal-catalyzed hydrophosphination of an alkyne is an alternative route to make those alkenylphosphines (Scheme 1-26). To the best of our knowledge, only a few examples of intramolecular reactions promoted by

organolanthanide complexes, together with some Pd, Rh, and Ni-catalyzed intermolecular reactions, have been reported.

Scheme 1-26

Scheme 1-27 shows the intramolecular hydrophosphination/cyclization of phosphinoalkynes catalyzed by organolanthanides.¹²⁰⁻¹²² Complexes such as $\text{Cp}^*_2\text{LnCH}(\text{TMS})_2$ ($\text{Ln} = \text{La}, \text{Sm}, \text{Y}$) and $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{t-BuN})\text{SmN}(\text{TMS})_2$ were found to be active precatalysts for these reactions, yielding the corresponding secondary phospholanes with very high conversion rates under mild reaction conditions. The reaction rate could be accelerated by increasing Ln^{3+} ionic radius as well as using the more open supporting ligand systems in the precatalyst.

Scheme 1-27

The intermolecular hydrophosphination of terminal and internal alkynes with Ph_2PH proceeded smoothly with regio and stereoselectivity in the presence of a ytterbium-imine

catalyst, $\text{Yb}(\eta^2\text{-Ph}_2\text{CNPh})(\text{hmpa})_3$, which was generated *in situ* from the Yb metal and the aromatic imine. The reaction rate was found to be extremely fast under mild reaction conditions for alkynes bearing phenyl groups, and the desired alkenylphosphineoxides were generated quantitatively through the consequent oxidative workup (Scheme 1-28).^{124, 125, 142} For aromatic alkynes, the PPh_2 group was exclusively introduced at the opposite side of the aryl substituent with preferential *E* stereochemistry. In contrast, for aliphatic alkynes, the regioselectivity was relative low and the stereochemistry was generally *Z*. Moreover, a mechanism involving the formation of a catalytic phosphide intermediate $[\text{Yb}]\text{-PPh}_2$, insertion of the alkyne into the Yb-P bond, and the regeneration of the catalyst by protonolysis with HPPH_2 was also suggested.^{124, 142}

Scheme 1-28

Other transition metal complexes such as $\text{Pd}(\text{PPh}_3)_4$, $\text{Pd}(\text{dba})_2$ (dba = dibenzylideneacetone), $\text{Pd}(\text{OAc})_2$, $\text{Ni}[\text{P}(\text{OEt})_3]_4$, $\text{Ni}(\text{acac})_2$ (acac = acetylacetonate), and

NiBr₂ are all active for hydrophosphination of alkynes. The regio and stereoselectivity is very much dependent on the catalyst and the substrate. For example, the addition of HPPH₂ to phenylacetylene led to the formation of the Ph₂P-CH=CHPh isomer regioselectively in the presence of Pd(PPh₃)₄. On the other hand, the Ph₂P-C(Ph)=CH₂ isomer was obtained when Ni(acac)₂/(EtO)₂P(O)H was used. High stereoselectivity (only *syn*-addition) could be obtained in the addition of HPPH₂ to 1,2-diphenylethyne catalyzed by Ni(acac)₂.¹⁴³ Furthermore, when catalyzed by Co(acac)₂ and butyllithium, a variety of alkynes reacted with HPPH₂ to generate exclusively *syn*-alkenylphosphines.¹¹⁸ In contrast, hydrophosphination of 1-alkynylphosphines with HPPH₂ proceeded in an *anti* fashion in the presence of a copper catalysis (CuI/Cs₂CO₃), providing an easy and efficient access to a variety of (*Z*)-1,2-diphosphino-1-alkenes.¹⁴⁴ Moreover, propargylic alcohols also underwent the addition of HPPH₂ catalyzed by a ruthenium complex. This reaction was different from other P-H addition reactions since it involved an external nucleophilic attack of HPPH₂ on the vinylidene ligand of the intermediate. The *Z/E* ratio depended on the structures of the substrate and the catalyst. Ru-Cp* (Cp* = η^5 -C₅Me₅) species selectively formed the *Z* isomer, while Ru-Cp (Cp = η^5 -C₅H₅) favored the *E* isomer. This catalytic process offered a method to prepare alkenylphosphines with hydroxyl functionality regioselectively.¹¹⁹

1.2.3 Transition Metal-Catalyzed Hydrophosphination of Formaldehyde

Acid-catalyzed addition of PH₃ to formaldehyde is an industrial process producing

$\text{P}(\text{CH}_2\text{OH})_4^+$, useful in preparing a flame retardant. As for the metal complex-catalyzed addition, various platinum compounds, such as PtCl_2 , PtCl_4 , $\text{K}_2[\text{PtCl}_4]$, $\text{Na}_2[\text{PtCl}_6]$, nickel, and cobalt salts in conjunction with primary and secondary amines have been reported to catalyze the addition of PH_3 to formaldehyde to generate tris(hydroxymethyl)phosphine since 1958 (Scheme 1-29).⁹⁴

Scheme 1-29

The catalytic transformation using aqueous CH_2O and PH_3 proceeded in the presence of $\text{K}_2[\text{PtCl}_4]$ at room temperature, forming a crystalline product in an essentially quantitative yield within 2.5 h.^{145, 146} Palladium and Nickel compounds are also active in this catalysis.¹⁴⁶ In these reactions the active species is believed to be zero valent. Two possible mechanisms have been proposed, as illustrated in Scheme 1-30. The first pathway includes the insertion of the $\text{C}=\text{O}$ bond into the $\text{M}-\text{H}$ species, while in the second pathway, a nucleophilic attack of the coordinating phosphide ligand on the formaldehyde forms a zwitterionic species.⁹⁴

Scheme 1-30

1.3 Metal-Catalyzed Hydration Reactions

Generally, a hydration reaction is a chemical reaction, in which a hydroxyl group (OH^-) and a proton are added to the two atoms bonded together in an unsaturated bond such as carbon-carbon double bond. This process generally proceeds in a strongly acidic, aqueous solution. The general chemical equation of the reaction is shown in Scheme 1-31.

Scheme 1-31

The well-known catalysts for hydration reactions are acid, enzyme, and transition metal complexes. Hydration, catalyzed by acid catalysts, generally proceeds to give the

Markovnikov product, but some sensitive functional groups are excluded from this acid-catalyzed reaction due to severe conditions used. Enzyme-catalyzed hydration is a very efficient process, but can be used for a limited range of substrates only. In contrast, transition metal complexes catalyze the hydration of a variety of substrates under relative mild conditions, yielding either Markovnikov or *anti*-Markovnikov products regioselectively.

1.3.1 Transition Metal-Catalyzed Hydration of Alkene

The addition of water to a carbon-carbon double bond is a potentially useful route for the synthesis of alcohols from alkenes (Scheme 1-31). Normally this process proceeds in the presence of acid catalysts.^{147, 148} For example, the large scale production of ethyl alcohol through the hydration of ethylene involves the use of an acid catalyst. The acids used as catalysts for this process include sulfuric acid, phosphoric acid, and a proton-exchanged zeolite.^{149, 150} However, these catalyzed reactions are of rather limited value when sensitive functional groups are present on alkenes due to both elevated temperature and high concentration of acids required for the hydration processes.

The addition of water to an alkene can also be accomplished by the use of mercuric acetate or borane. In principle, an unsymmetrical alkyl-substituted carbon-carbon double bond during a hydration reaction can form an alcohol product regioselectively, which depends on the mode of hydration in a Markovnikov and in an *anti*-Markovnikov manner, respectively. In general, the oxymercuration-demercuration of alkenes provides a very

efficient method for the Markovnikov addition. In those reactions with mercuric acetate, it is believed that an initial electrophilic attack on the alkene followed by reduction of the organomercurial intermediate gives the product alcohol (Scheme 1-32). On the other hand, hydroboration-oxidation leads to an *anti*-Markovnikov hydration. Recently, various combinations of Lewis acids and borohydrides such as $\text{Me}_3\text{SiCl-PhCH}_2\text{N}^+(\text{Et})_3\text{BH}_4^-$,¹⁵¹ $\text{TiCl}_4\text{-PhCH}_2\text{N}^+(\text{Et})_3\text{BH}_4^-$,¹⁵² $\text{SnCl}_4\text{-NaBH}_4$,¹⁵³ $\text{TiCl}_4\text{-NaBH}_4$,¹⁵⁴ $\text{CoCl}_2\text{-NaBH}_4$,¹⁵⁵ and $\text{Zn(BH}_4)_2\text{-silica gel}$ have been reported to be efficient for this process.¹⁵⁶

Scheme 1-32

Transition metal complexes have been utilized to affect the homogeneous hydration of electron deficient alkenes. For the hydration reactions of fluoro substituted alkenes, solutions containing chlororuthenate(II) species have been used as catalysts. The mechanism of the chlororuthenate(II)-catalyzed reaction is proposed to involve the insertion of the carbon-carbon double bond of the alkene into the the ruthenium-hydroxide bond (Scheme 1-33).¹⁵⁷ Moreover, various compounds of aluminum(III) and chromium(III) have also been reported to catalyze the hydrations of fumaric and maleic acid.

Scheme 1-33

Pd and Pt complexes with catalytic activity in olefin hydrations have also been developed. Di- η -hydroxo complexes, $[Pd_2(\eta^2-OH)_2(L_2)_2]^{2+}$ ($L_2 = dppe, dcpe$), catalyzed the hydration of diethyl maleate to give diethyl malate, though with low turnover number.^{158, 159} Acyclic 1,3-dienes, such as butadiene and isoprene, underwent an addition of water to form octadienols as well as tail-to-tail dimerization in the presence of palladium catalysts such as $Pd(acac)_2/PPh_3$ or $Pd(PPh_3)_4$. Under similar conditions,¹⁶⁰⁻¹⁶² the hydration of allene generated 3-methyl-2-methylene-3-buten-1-ol.¹⁶³ Furthermore, tetrafluoroethylene and dimethyl maleate were observed to insert into the Pt-O bond,¹⁶⁴⁻¹⁶⁶ which indicated the potential of Pt complexes in catalyzing olefin hydrations.¹⁶⁷ The direct *anti*-Markovnikov hydration of terminal alkenes was observed to be catalyzed by *trans*- $PtHCl(PMe_3)_2$ in the presence of aqueous NaOH and a phase-transfer catalyst at 60-100 °C,¹⁶⁸ but unfortunately this process was proved to be irreproducible.¹⁶⁹

1.3.2 Transition Metal-Catalyzed Hydration of Alkyne

Hydration of alkynes is one of the simplest and the most convenient ways to obtain carbonyl compounds. For a long time the hydration of acetylene has been a reaction of major industrial interest. In fact, before the advent of the Wacker process, acetaldehyde was essentially produced by the hydration of acetylene. Other alkynes give ketones in almost all cases, i.e., hydration of alkynes of the type $\text{RC}\equiv\text{CH}$ formed methyl ketones almost exclusively (Scheme 1-34), while for alkynes of the type $\text{RC}\equiv\text{CR}'$, both regioisomers could be obtained.⁹⁵

Scheme 1-34

The hydration of alkynes can be catalyzed by acid catalysts, but the rate was often slow except for those very reactive alkynes.¹⁷⁰ However, this process was found to be accelerated by a wide variety of mercury(II) compounds in aqueous acid solutions.¹⁷¹⁻¹⁷³ Furthermore, ion-exchange resins¹⁷⁴⁻¹⁷⁷ containing Hg(II) or other ions such as Cu(I), Zn(II), and Cd(II), many metal phosphates, transition metal phosphomolybdates,¹⁷⁸ heteropoly acids (HPAs),^{179, 180} and zeolite catalysts containing a variety of transition metal ions^{170, 181} are also effective catalysts for an alkyne hydration.

Many late transition metal complexes have also been used as catalysts for hydration of an alkyne.¹⁸² For example, RuCl_3 is an effective catalyst for the hydration of acetylene

and mono and disubstituted alkynes under relatively mild reaction conditions. Methyl acetylene, ethylacetylene, and phenylpropionic acid could be converted into acetone, ethyl methyl ketone, and acetophenone, respectively, through the corresponding processes. It was suggested that water was delivered from the coordination sphere of ruthenium in a π -complex to the activated carbon-carbon triple bond before protonolysis (Scheme 1-35).¹⁸³ Moreover, A water-soluble complex $\text{K}[\text{Ru}(\text{III})(\text{EDTA}-\text{H})\text{Cl}]\cdot 2\text{H}_2\text{O}$ was also observed to catalyze the hydration of acetylene to give acetaldehyde.¹⁸⁴ Many other Ru complexes, such as $\text{Ru}_3(\text{CO})_{12}$,¹⁸⁵ $\text{CpRu}(\text{COD})\text{Cl}$,¹⁸⁶ indenyl complex $(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\text{COD})\text{Cl}$,¹⁸⁷ and $\text{RuCl}_2(\eta^6\text{-arene})\text{-}\{\text{P}(\text{CH}_2\text{OH})_3\}$ ¹⁸⁸ also have catalytic activity in the alkyne hydration.

Scheme 1-35

Apart from ruthenium complexes, other transition metal complexes have also been reported to catalyze alkyne hydration reactions. For example, $\text{RhCl}_3\cdot 3\text{H}_2\text{O}$ ¹⁸⁹ and ion pairs^{190, 191} generated from $\text{RhCl}_3\cdot 3\text{H}_2\text{O}$ are both effective catalysts, and the latter could be recovered as NaRhCl_4 in the aqueous phase by treatment with aqueous NaClO_4 . Electron deficient substrates, such as dimethyl acetylenedicarboxylate, underwent a *trans*-addition of water in the presence of *cis*- $[\text{Pd}(\text{PhPMe}_2)_2\text{Cl}_2]$ to give oxalacetic acid

dimethyl ester, which exists predominantly in the enol form.¹⁹² The hydration reactions of many terminal or internal alkynes bearing other functional groups such as carbonyl, hydroxyl group, or carbon-carbon double bond were also found to be catalyzed by Pd(II),¹⁹³⁻¹⁹⁶ Pt(II),¹⁹⁷⁻²⁰¹ or Pt(IV)²⁰²⁻²⁰⁴ complexes to give the corresponding products regioselectively. Additionally, other catalysts containing transition metals include Ir, Cu,¹⁹³ and Au^{195, 205-209} complexes. It is noteworthy that most of hydrations proceeded in a Markovnikov manner and generated ketones. For example, Au(I)-acid catalytic system in aqueous methanol is a powerful catalyst to promote the hydration reactions of a variety of terminal alkynes to form the Markovnikov products exclusively (Scheme 1-36).²⁰⁸

Scheme 1-36

Scheme 1-37

Interestingly, *anti*-Markovnikov products of alkyne hydration reactions could be obtained in the presence of some Ru catalysts.²¹⁰⁻²¹⁸ For instance, the reaction of 1-hexyne with water in the presence of 1 mol % CpRu(dppm)Cl in 2-propanol at 100 °C

for 12 h gave hexanal quantitatively without any by-product (Scheme 1-37).²¹² Insight into the reaction mechanism indicated that the resulting formyl hydrogen came from the original acetylenic hydrogen and that the Ru(II)-vinylidene species were not involved in the pathway. The proposed mechanism includes (a) proton attack from water at the substituted carbon of a Ru(II)- η^2 -coordinated alkyne, (b) α -hydrogen migration to the metal center to form a Ru(IV)-hydride-vinylidene intermediate, (c) attack of the hydroxyl anion at the α -carbon of the vinylidene, and (d) reductive coupling of the resulting acyl group and hydride to give the aldehyde and the Ru(II) species (Scheme 1-38).²¹³ Furthermore, since Ru catalysts could lead to the formation of both Markovnikov and *anti*-Markovnikov products, an elegant method to control the regioselectivity in the addition of water across terminal alkynes has been developed. The presence of the π -acidic COD ligand in the indenyl ruthenium(II) complex $(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\text{COD})\text{Cl}$ favored a π -alkyne intermediate that directed the addition of water in a Markovnikov fashion.¹⁸⁷ In contrast, the electron rich bisphosphine complex $(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\text{PPh}_3)_2\text{Cl}$, which favored a vinylidene intermediate, drove the addition of water to both terminal alkynes and propargyl alcohols in an *anti*-Markovnikov manner, when the reaction was performed at 60 °C in an aqueous micellar environment.²¹⁶

In conclusion, the formation of Markovnikov or *anti*-Markovnikov products depends on the intermediate generated in the hydration process. The π -alkyne intermediate could lead to the formation of Markovnikov products. For most metal catalysts, this regioselectivity has been observed in the corresponding cases. However, the generation of the vinylidene intermediate will lead to the formation of

anti-Markovnikov products. To the best of our knowledge, only hydration reactions in the presence of those ruthenium catalysts containing electron rich ligands proceeded in an *anti*-Markovnikov manner.

Scheme 1-38

The regioselective hydration of internal alkynes could also be achieved in the presence of a directing functionality.^{194-196, 199-201, 219-221} For example, the Au(III)-catalyzed hydration of 3-alkynoates led to the generation of γ -keto esters in high yield, through a carbonyl group participation enabled by a favored 5-*endo-dig* cyclization (Scheme 1-39).²¹⁹

Scheme 1-39

1.3.3 Transition Metal-Catalyzed Hydration of Nitrile

Hydration of nitriles to prepare amides is an important reaction in the laboratory and in industry. The mechanism is shown in Scheme 1-40a. Both proton and hydroxy ion can promote this process, since the proton interacts with the nitrogen atom to accelerate the polarization of the carbon-nitrogen bond, while hydroxy ion behaves as a nucleophile to react with the carbon atom.¹⁷⁰

Hydration of nitrile could be catalyzed by various acids²²² and bases,²²³ but many of these classical methods required harsh conditions and gave low yields. Furthermore, the undesirable further hydrolysis of amides into carboxylic acids could not be avoided, since the rate of hydrolysis was faster than that of hydration, especially under basic conditions (Scheme 1-40b).²²⁴ Another limitation of the classical methods is that acid- or base-sensitive functional groups cannot be incorporated into the substrates since harsh

conditions, i.e., strong acids or bases, are required in the reactions due to the low reactivity of the nitrile group. To overcome these defects, a number of methods based on improved acidic and basic catalytic systems,²²⁵⁻²²⁹ heterogenous catalysts,²³⁰⁻²³² solvent free system,²³³ enzymes,^{234, 235} and transition metal catalysts have been developed.

(a)

(b)

Scheme 1-40

A variety of transition metal complexes, such as Pd(II),²³⁶⁻²⁴¹ Pt(II),^{224, 242-245} Pt(0),^{246, 247} Ru(II),²⁴⁸⁻²⁵¹ Ir(III),²⁵² Rh(I),²⁵³ Ni(II),^{254, 255} Fe(II),²⁵⁵ Cu(II),^{254, 255} Co(II),²⁵⁵ Co(III),^{256, 257} Zn(II),^{254, 258} and Mo(IV) complexes,^{259, 260} have been reported to have catalytic activity in nitrile hydrations. A well-known mechanism for the transition metal-catalyzed conversion of a nitrile into an amide involves an intramolecular nucleophilic attack of a hydroxo ligand or the external attack of a hydroxide ion on the carbon atom of the η^1 -coordinated nitrile molecule and the subsequent protonation of the nitrogen atom (Scheme 1-41).^{237, 245, 256, 260} In a palladium-catalyzed hydration reaction,

on the basis of kinetic experiments, it was proposed that the amide was formed through both internal and external attack of the neighboring aqua ligand and the solvent water, respectively, which occurred at similar rates, on the nitrile ligand.²³⁷

external attack

internal attack

Scheme 1-41

One of the most efficient catalysts for hydration of nitriles to amides is the homogeneous platinum phosphinito complex, $[PtH-(PMe_2OH)(PMe_2O)_2H]$. The turnover frequency and turnover number of catalytic hydration of acetonitrile reached 380 h^{-1} and 5700, respectively. The cationic nitrile complex $[Pt(RCN)(PMe_2OH)(PMe_2O)_2H]^+$ was believed to be the active species responsible for the catalysis. This hydration process is thought to begin by an intramolecular nucleophilic attack of the PMe_2OH hydroxyl on the carbon center of the nitrile ligand, forming an intermediate that contained a

five-membered ring iminol-type ligand. The addition of a H₂O molecule across the C=N bond of the iminol-type ligand followed by the subsequent proton transfer yielded the amide. Moreover, coordination of another nitrile to the metal center regenerated the active species (Scheme 1-42).^{242, 243}

Hydration of acrylonitrile to yield acrylamide selectively remains challenge in organic synthesis since β -cyanoethanol and β -dicyanoethyl ether are often formed as by-products (Scheme 1-43). Pt and Mo complexes have been found to catalyze the hydration of the nitrile moiety rather than the alkenyl group in acrylonitrile with high selectivity of more than 97%.^{243, 245, 260} The best selectivity was more than 99%.^{243, 260}

Scheme 1-42

Scheme 1-43

1.4 Metal-Catalyzed Hydroamination

A formal addition of an N-H bond across carbon-carbon unsaturated bonds, collectively known as hydroamination, has gained a great deal of attention as a simple and atom-economical protocol for N-functionalization (Scheme 1-44). Direct addition of nucleophiles, H-NR₂, to activated alkenes proceeded in an *anti*-Markovnikov manner to generate compounds with nitrogen atoms β to a functional groups such as keto, ester, nitrile, sulfoxide, or nitro. On the other hand, hydroaminations of aliphatic olefins and most aromatic olefins were observed to yield Markovnikov products.²⁶¹

Scheme 1-44

Two basic approaches involving either alkene/alkyne or amine activation routes have been employed to catalytically effect aminations (Scheme 1-45).²⁶¹ Alkene activation is generally accomplished with late transition metal catalysts, which render coordinated olefins more susceptible to attack by exogenous amine nucleophiles. Intermediate 2-aminoalkyl complexes can then react in different ways, leading to the formation of oxidative amination, hydroamination, or polyfunctionalized products. Like alkenes, alkynes can also be activated by coordination to a late transition metal center. On the other hand, alkali metals can be used to activate amines through the generation of a highly nucleophilic amido species, which is then able to attack the alkene directly. An alternative amine activation route uses the N-H oxidative addition to electron rich late transition metal centers. A catalytic cycle for olefin hydroamination can be realized if the oxidative addition step is coupled to an alkene/alkyne insertion process followed by the reductive elimination of the product.

Alkene Activation

Amine Activation

Scheme 1-45

1.4.1 Transition Metal-Catalyzed Hydroamination of Alkene

In the presence of a stoichiometric amount of K_2PtCl_4 , 1-amino- n -alkenes ($n = 4, 5$) underwent cyclization in aqueous solution at 60°C .^{262, 263} An acidic medium and the presence of additional chloride ions were required to prevent the separation of metallic platinum. However, the slow rate of these reactions precludes the further synthetic exploitation. These intramolecular cyclizations of aliphatic aminoalkenes could also be catalyzed by organolanthanide complexes.²⁶⁴⁻²⁶⁷ The complexes $(\text{Me}_5\text{C}_5)_2\text{LnR}$ and $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)_2\text{LnR}$ ($\text{Ln} = \text{La, Nd, Sm, Y, Lu}$; $\text{R} = \text{H}, \eta^3\text{-allyl}, \text{E}(\text{SiMe}_3)_2$ with $\text{E} = \text{CH, N}$) catalyzed the intramolecular hydroamination of primary and secondary tethered

aminoalkenes to yield the corresponding 2-methyl heterocycles (Scheme 1-46). Under mild conditions, five-, six-, and seven-membered cyclic amines were formed in products with high regioselectivity. Moreover, hydroaminations of unactivated olefins with primary and secondary alkylamines were observed to be catalyzed by rhodium complexes to form the corresponding five- and six-membered cyclic products in excellent yields. The reactions formed exclusively the products resulting from hydroamination, rather than the competitive oxidative amination or olefin isomerization, in the presence of catalysts generated from $[\text{Rh}(\text{COD})_2]\text{BF}_4$ and a biaryl dialkyl phosphine or an analogue of Xantphos [9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene].²⁶⁸

Scheme 1-46

There are also several literature examples that reported intermolecular hydroaminations of alkenes. Pd catalysts were found to catalyze the addition of aromatic amines to vinylarenes in a Markovnikov manner. For example, combination of $\text{Pd}(\text{PPh}_3)_4$ and triflic acid co-catalyst and the combination of DPPF [DPPF = 1,1'-bis(diphenylphosphino)ferrocene], palladium trifluoroacetate and triflic acid were

reported to catalyze the additions of a variety of anilines to several types of vinylarenes (Scheme 1-47).²⁶⁹ Generally, the high yields were obtained in the reactions with electron rich anilines, while the reactions involving electron poor anilines occurred in relative low yields. However, the reactions with the electron poor vinylarenes, such as trifluoromethylstyrene and vinylnaphthalene, occurred with a fast rate and in high yield. Recently, catalysts generated from $[\text{Pd}(\eta^3\text{-allyl})\text{Cl}]_2$ (with or without added AgOTf) or $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ and Xantphos have been reported to be very active for the intermolecular hydroamination of vinylarenes. Furthermore, these reactions could also be performed even in the presence of potentially reactive functional groups on the anilines, such as ketones with enolizable hydrogens, free alcohols, free carboxylic acids, free amides, nitriles, and esters.²⁷⁰ The mechanism of these hydroaminations was proposed to proceed via the formation of a η^3 -phenethyl complex and the further external attack of the amine on the benzylic carbon.²⁷¹

Scheme 1-47

The first example of a transition metal-catalyzed hydroamination of an olefin in *anti*-Markovnikov manner is the reaction of morpholine with styrene in the presence of 2.5% $[\text{Rh}(\text{COD})_2]\text{BF}_4$ and PPh_3 . However, the major product was the undesired enamine product, which arose from an oxidative amination pathway.²⁷² Moreover, the

anti-Markovnikov addition of alkylamines to vinylarenes catalyzed by [Rh(COD)(DPEphos)]BF₄ has also been reported (Scheme 1-48).²⁷³ This process proceeded through the first amination of an olefin to form the terminal amines as the major product. This bis-diphenylphosphinophenyl ether is far unique for forming this *anti*-Markovnikov hydroamination product in good yield. In these reactions, the by-product enamines also formed as oxidative amination product. Reactions of the electron neutral or the electron rich vinylarenes occurred with high ratios for the formation of the hydroamination to oxidative amination products, although these reactions were slower than those involving electron poor vinylarenes. In contrast, the reactions with electron poor vinylarenes gave lower ratios of the hydroamination to oxidative amination products. In addition, higher concentration of the styrene was also found to generate the lower ratio of amines to enamines. Apart from rhodium complexes, ruthenium catalysts have also been developed. For example, the combination of Ru(COD)(2-methylallyl)₂, 1,5-bis(diphenylphosphino)pentane, and triflic acid was the most effective catalyst for the hydroamination reactions of vinylarenes with secondary aliphatic and benzylic amines through an *anti*-Markovnikov pathway.²⁷⁴ The reaction of morpholine, piperidine, 4-phenylpiperazine, 4-BOC-piperazine, 4-piperidone ethylene ketal, and tetrahydroisoquinoline with styrene in the presence of 5 mol % of this catalyst formed the corresponding β -phenethylamine products in 64–96% yield, with 99% regioselectivity, and without enamine by-products. The mechanism of the ruthenium-catalyzed hydroamination is distinct from that of the rhodium-catalyzed reaction.²⁷⁵

Scheme 1-48

Stereoselectivity has also been achieved by using the chiral ligands in both intra and intermolecular cases. For example, the complexes $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{R}^*\text{H}_3\text{C}_5)\text{LnE}(\text{SiMe}_3)_2$ ($\text{E} = \text{CH}, \text{N}$; $\text{R}^* = \text{menthyl, neomenthyl}$) containing a chiral center catalyzed hydroamination of 1-amino-4-pentenes to yield 2-methylpyrrolidines enantioselectively.²⁶⁴ The lower reaction temperature, the better enantioselectivity. Diastereoselective processes could also be influenced by chiral lanthanide complexes. The cyclization of 2-amino-5-hexenes yielded *trans*-2,5-dimethylpyrrolidines with more than 95% diastereoselectivities (Scheme 1-46).²⁶⁷ Additionally, when catalyzed by a palladium complex bearing BINAP, the intermolecular addition of aniline to trifluoromethylstyrene proceeded in 81% yield and with 81% enantioselectivity.²⁷⁶

Hydroamination of dienes can lead to the formation of allylic amines. The reaction, using Pd catalyst, coupled aromatic amines with dienes successfully (Scheme 1-49). Both electron rich and electron deficient aromatic amines could react with cyclohexadiene in good to excellent yields (78-99%) under mild reaction conditions.²⁷⁷ Furthermore, the

hydroamination of aliphatic amine was favored to be catalyzed by Ni(0) catalyst efficiently. Good yields (56-94%) have been gained for most primary and secondary amines except those extremely hindered amines, such as dicyclohexylamine.²⁷⁸

Scheme 1-49

1.4.2 Transition Metal-Catalyzed Hydroamination of Alkyne

The hydroamination of alkynes is a fundamental reaction in organic synthesis which allows, in a straightforward manner, the preparation of valuable nitrogen-containing compounds, such as enamines and imines. A variety of catalytic and noncatalytic methods, including thermal-, acid-, base-promoted and transition metal-catalyzed reactions,²⁷⁹ have been developed to overcome the high activation energy required for this process. However, there are still not any general and simple methods (particularly on an industrial scale) that can be applied in cases of all alkynes and amines.⁹⁵

Tethered aminoalkynes could be cyclized to give hydroamination products using titanium, nickel, palladium, gold, and lanthanide complexes as catalysts. One catalyst employed is Ni(CO)₂(PPh₃)₂ that allowed the cyclization of 1-amino-3-alkynes and 1-amino-4-alkynes to form 1-pyrrolines in moderate yields.²⁸⁰ The formation of 1-pyrrolines with both substrates demonstrated the preferential formation of a

five-membered ring, which had also been observed in cases of other transition metal catalysts. For the cyclization of 1-amino-5-alkynes, $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ is active to convert the substrates into 3,4,5,6-tetrahydropyridines with nearly quantitative yield.²⁸¹ Catalytic palladium chloride in acetonitrile was also reported to catalyze the cyclization of 1-amino-5-alkynes to generate the corresponding hydroxyridines with moderate yields (42-72%).²⁸² Furthermore, the intramolecular hydroamination of aminoalkynes could also be effected by lanthanide complexes, such as $(\text{Me}_5\text{C}_5)_2\text{LnCH}(\text{SiMe}_3)_2$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Lu}$) and $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)_2\text{LnCH}(\text{SiMe}_3)_2$ ($\text{Ln} = \text{Nd}, \text{Sm}$).^{283, 284} These catalysts could be utilized in lower concentration (~ 0.5 mol %) than late transition metal catalysts, and in most cases improved yields (85-95%) were obtained. Moreover, in those processes catalyzed by lanthanide complexes, five-, six-, and seven-membered heterocycles were regiospecifically formed from substrates bearing various substituents on the alkyne moiety ($\text{R} = \text{H}, \text{alkyl}, \text{Ph}, \text{SiMe}_3, \text{allyl}$). Cyclization rates were influenced considerably by the substituent on the alkyne moiety with $\text{SiMe}_3 > \text{H} > \text{Me} > \text{Ph}$ and showed a strong ring size dependence with $5 > 6 \gg 7$. Electron rich π -systems are more facile to be cyclized, e.g., the cyclization of $\text{H}_2\text{N}(\text{CH}_2)_3\text{C}\equiv\text{CSiMe}_3$ with $(\text{Me}_5\text{C}_5)\text{SmCH}(\text{SiMe}_3)_2$ proceeded quantitatively and turnover frequencies was found to be more than 7600 h^{-1} at 21°C (Scheme 1-50).²⁶¹

Scheme 1-50

Intermolecular hydroamination of alkynes could proceed through both Markovnikov and *anti*-Markovnikov pathways, when catalyzed by transition metal complexes. For example, Ti complexes were found to be efficient catalysts for this hydroamination process to generate both regioselective products, depending on the ligands of the involved complexes. The Ti complexes with amine ligands catalyzed the hydroamination of terminal alkynes in a Markovnikov manner,²⁸⁵⁻²⁸⁸ while those with Cp and amidate ligands promoted reactions to form *anti*-Markovnikov products.²⁸⁹⁻²⁹³ Regioselective hydroamination of terminal alkynes have also been reported in the reaction catalyzed by $\text{Cp}^*_2\text{U}\text{Me}_2$.²⁹⁴ This reaction allowed relatively low concentration of the catalyst to be used and gave the *anti*-Markovnikov product with yields up to 95%. In contrast, when the corresponding thorium complex, $\text{Cp}^*_2\text{Th}\text{Me}_2$, was used, the regioselectivity of the addition of phenyl acetylene was reversed, yielding the Markovnikov product, 1-phenyl iminoethane (Scheme 1-51). Moreover, the late transition metal complexes such as $\text{Ru}_3(\text{CO})_{12}$ ²⁹⁵ and $[\text{Rh}(\text{COD})_2]\text{BF}_4$ ²⁹⁶ could also catalyzed the hydroamination reactions of terminal alkynes with Markovnikov regiochemistry. On the other hand, internal alkynes have also been reported to undergo hydroamination using zirconocene bisamides $\text{Cp}_2\text{Zr}(\text{NHR})_2$ as catalysts.^{297, 298} Primary aromatic amines reacted with 2-butyne to yield N-substituted 2-iminobutane and diphenyl-1-aminoethene. The isomerization of the latter to give the corresponding imine was not observed since the conjugation of the double bond with the phenyl groups stabilized the product as an enamine. The investigation of mechanism revealed that an azametallacyclobutene intermediate was included in the catalytic cycle.

Scheme 1-51

1.5 Aims of the Present Project

Our group has been interested in the asymmetric syntheses of chiral phosphines by means of metal template-promoted reactions. Aided by the Pd or Pt complexes containing the chiral auxiliary 1-(dimethylamino)ethylnaphthalene, a variety of chiral phosphine and arsine ligands were obtained in high stereoselectivities by the corresponding reactions including [4+2] and [2+2] cycloaddition, hydrophosphination, hydroamination, and hydroarsination. Through functionalization of one C=C bond in dialkenylphosphine (or one C≡C bond in dialkynylphosphine), the P-chirality could be successfully induced. It is noteworthy that the remaining unreacted olefin or alkyne moiety in these products may not be a functionally valuable substituent, although the P-chiral center is formed stereoselectively. However, this alkenyl or alkynyl group should still be reactive towards further organic or organometallic reactions and is available to be further functionalized. This project not only aims at the investigation of the generation of a stereogenic phosphorus through functionalization of one alkyne moiety in a dialkynylphosphine complex but also explores the further functionalization of the remaining unreacted alkynyl group to form the bifunctionalized phosphine complexes.

In this project work, (η^6 -benzene)ruthenium complexes bearing alkynylphosphine exhibited high reactivities. After coordination of prochiral diprop-1-ynylphenyl phosphine [$\text{PhP}(\text{C}\equiv\text{CMe})_2$] to ruthenium, the two alkyne moieties in the phosphine ligand underwent hydrophosphination, insertion, hydration, or hydroamination smoothly under mild reaction conditions. The reactivities, regio- and stereoselectivities of these reactions have been studied. Furthermore, interesting structural features were observed with the generated bifunctionalized phosphine complexes, which have been confirmed by X-ray crystallographic analyses in the solid state and 2D ROESY NMR studies in solution.

Chapter 2

Ruthenium Promoted Hydrophosphination of Dialkynylphosphine and the Subsequent Insertion into Pd-C bond of Cyclopalladated Complex

2.1 Introduction

Syntheses of phosphine ligands and their coordinated metal complexes have received considerable attention because of the important roles they play as biological active compounds and organic catalysts. Hydrophosphination, as an efficient and atom economical method, has become a powerful tool to form the P-C bond. The classic processes proceed by thermal,⁹⁶⁻⁹⁸ acidic,^{99, 100} basic,¹⁰¹⁻¹⁰⁴ or free radical¹⁰⁵⁻¹¹⁰ pathways. However, the use of transition metal complexes for such reactions often offers vast improvement in rate, selectivity, and stereocontrol. Apart from catalytic processes, there are examples of hydrophosphination reactions that are promoted by stoichiometric quantities of transition metal complexes.¹²⁷⁻¹³⁷

Diphosphines can be synthesized via hydrophosphination reactions through two pathways. The first is via hydrophosphination of the olefin or alkyne moiety in an alkenyl- or alkynylphosphine;¹⁴⁴ the second is the reaction of an alkyne with 2 equiv of diphenylphosphine.¹³³ Furthermore, to synthesize chiral phosphine bearing C- or P-chirality, asymmetric hydrophosphination involving chiral auxiliaries on the metal

have also been utilized. For example, using the chiral amine as the auxiliary on palladium to synthesize C-chiral dimethyl-1,2-bis-(diphenylphosphino)-1,2-ethanedicarboxylate, the $R_C R_C$ and $S_C S_C$ products formed with a ratio of 6:1.¹³³ The iron complexes bearing chiral bis(phosphine) ligands $\{C_5H_5(diphos)Fe[P(R)H_2]\}BF_4$ (diphos = DIOP, CHIRAPHOS) have also been used to provide stereocontrol of the hydrophosphination process involving primary phosphine (PRH₂) and olefin, therefore yielding the P-chiral phosphine (Scheme 2-1).¹³⁶

Formation of C-chiral Phosphine Ligand

Formation of P-chiral Phosphine Ligand

Scheme 2-1

Another important strategy to generate a P-chiral center includes stereoselective functionalization of a prochiral phosphine bearing two similar functional groups such as

dialkenyl or dialkynyl groups. For example, the dialkenylphenylphosphine, after coordination to the chiral palladium template, underwent the Diels-Alder reaction with DMPP (3,4-dimethyl-1-phenylphosphole) to give one of the two possible diastereoisomers (Scheme 2-2).²⁹⁹⁻³⁰¹ The newly generated bicyclo[2.2.1] group, phenyl group, and the remaining alkenyl group led to the generation of a stereogenic center at phosphorus. However, this strategy still remains to be further investigated for the preparation of chiral diphosphines. Diphosphines bearing a P-chiral center can be synthesized through hydrophosphination of a dialkenyl- or dialkynylphosphine with diphenylphosphine. Moreover, the remaining unreacted group should still be reactive toward further organic or organometallic reactions and is available to be further functionalized to form another substituent (Scheme 2-3). It is noteworthy that, using this synthetic strategy, the absolute configuration at phosphorus is expected to be retained in the bifunctionalized phosphine.

Scheme 2-2

Scheme 2-3

Insertion of an alkyne into the Pd-C bond in a palladacycle involving benzylamine and its analogues exhibits high reactivity.³⁰²⁻³⁰⁵ Recently, our group studied insertion reactions of P-coordinated alkynylphosphine complexes with cyclopalladated complexes.³⁰⁶ Coordination of an alkynylphosphine to palladium or platinum center successfully induced the activation of the alkyne moiety, which sequentially underwent insertions into Pd-C bonds of various cyclopalladated complexes involving benzylamines with high reactivities. In the present project work, an insertion reaction was utilized for functionalization of the remaining unreacted alkyne moiety of the hydrophosphination product (Scheme 2-3).

2.2 Results and Discussion

2.2.1 Preparation of Phosphine Ligand 1

The dialkynylphosphine ligand $\text{PhP}(\text{C}\equiv\text{CCH}_3)_2$ **1** could be readily prepared through the reaction of 2 equiv of alkynyl-Grignard, $\text{BrMg-C}\equiv\text{CCH}_3$, with dichlorophenylphosphine Cl_2PPh (Scheme 2-4). After being stirred overnight, the

reaction mixture was neutralized, and then extracted with diethyl ether. Removal of organic solvent gave the crude product. The pure product was obtained by microdistillation as a colorless liquid of the crude product in 63% yield. In CDCl_3 , the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for ligand **1** shows a singlet signal at δ -59.7.

Scheme 2-4

2.2.2 Preparation of Precursor Complexes **3** and **5**

Using a modified literature method,³⁰⁷ the P-coordinated precursor complexes **3** and **5** were prepared. Commercially available complex $[(\eta^6\text{-benzene})\text{RuCl}_2]_2$ **2** was treated with phosphine ligand **1** at room temperature in acetone to give a reddish-brown suspension that was then left to stir vigorously for 1 day. The color of the suspension changed into reddish-orange after the coordination process. Removal of solvent gave the product **3** as an orange powder in 97% yield. The product was essentially pure and could be used directly for the subsequent reactions without further purification. In CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3** showed a singlet at δ -20.2. Recrystallization of complex **3** from chloroform and diethyl ether gave red needles. It is noteworthy that in CDCl_3 , the two identical methyl groups of **3** showed a doublet at δ 2.12 ($^4J_{\text{PH}} = 3.8$ Hz) in the ^1H NMR spectrum.

Scheme 2-5

The monoalkynylphosphine **4** was prepared through a similar process as for the synthesis of ligand **1**. Complex $[(\eta^6\text{-benzene})\text{RuCl}_2]_2$ (**2**) was treated with phosphine ligand **4** at room temperature in acetone. The resulting reddish-brown suspension was then left to stir vigorously overnight, after which the color of the suspension changed into reddish-orange. Removal of solvent gave the product **5** as an orange powder in 98% yield. The product was essentially pure and could be used directly for the subsequent reactions without further purification. In CDCl_3 , the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** showed a singlet at δ 0.1. Recrystallization of complex **5** from dichloromethane and diethyl ether gave red needles.

2.2.2.1 X-ray Structural Analysis of Complex 3

The single crystal X-ray structure of the ruthenium complex **3** is shown in Figure 2-1. Complex **3** has the "three-legged piano-stool" geometry, the η^6 -coordinated arene is

in a "stool" position, while the "legs" comprise P and Cl atoms. The angles at the Ru center and the P center are in the range of 85.8(2)-87.3(2)° and 102.9(1)-119.5(1)°, respectively. Selected bond distances and angles for complex **3** are given in Table 2-1.

Figure 2-1 Molecular structure of complex **3**

Table 2-1 Selected Bond Lengths (Å) and Angles (deg) of **3**

Ru(1)-P(1)	2.308(1)	Ru(1)-Cl(1)	2.412(1)
Ru(1)-Cl(2)	2.394(1)	P(1)-C(7)	1.759(2)
P(1)-C(10)	1.748(2)	P(1)-C(13)	1.826(2)
C(7)-C(8)	1.186(3)	C(10)-C(11)	1.197(3)
P(1)-Ru(1)-Cl(1)	87.0(2)	P(1)-Ru(1)-Cl(2)	85.8(2)
Cl(1)-Ru(1)-Cl(2)	87.3(2)	C(7)-P(1)-Ru(1)	112.0(1)
C(10)-P(1)-Ru(1)	119.5(1)	C(13)-P(1)-Ru(1)	113.2(1)

C(7)-P(1)-C(13)	103.6(1)	C(10)-P(1)-C(7)	102.9(1)
C(10)-P(1)-C(13)	103.9(1)		

2.2.2.2 X-ray Structural Analysis of Complex 5

The single crystal X-ray structure of the ruthenium complex **5** is shown in Figure 2-2. Like complex **3**, complex **5** also has the "three-legged piano-stool" geometry, the η^6 -coordinated arene is in a "stool" position, while the "legs" comprise P and Cl atoms. The angles at the Ru center and the P center are in the range of 86.3(1)-90.5(1)° and 103.9(3)-124.1(1)°, respectively. Selected bond distances and angles for complex **5** are given in Table 2-2.

Figure 2-2 Molecular structure of complex **5**

Table 2-2 Selected Bond Lengths (Å) and Angles (deg) of **5**

Ru(1)-P(1)	2.322(1)	Ru(1)-Cl(1)	2.405(1)
Ru(1)-Cl(2)	2.418(1)	P(1)-C(7)	1.775(9)
P(1)-C(10)	1.793(1)	P(1)-C(16)	1.829(4)
C(7)-C(8)	1.190(1)		
P(1)-Ru(1)-Cl(1)	86.3(1)	P(1)-Ru(1)-Cl(2)	88.3(1)
Cl(1)-Ru(1)-Cl(2)	90.5(1)	C(7)-P(1)-Ru(1)	109.6(3)
C(10)-P(1)-Ru(1)	108.5(5)	C(16)-P(1)-Ru(1)	124.1(1)
C(7)-P(1)-C(16)	103.9(3)	C(10)-P(1)-C(7)	103.9(5)
C(10)-P(1)-C(16)	105.0(6)		

2.2.3 Preparation of Intermediate Complex **6**

The intermolecular hydrophosphination of complex **3** and free diphenylphosphine was found to be very slow when the reaction was monitored by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. However, coordination of HPPH_2 to the ruthenium center of complex **3** should dramatically accelerate the P-H addition process. This strategy has been also widely used in syntheses of phosphine complexes promoted by cyclopalladated or cycloplatinated complexes.²⁹⁹ Since the Ru-Cl bond in complex **3** is kinetically stable, the anionic chloride ligand is inert to ligand exchange reactions even in the presence of

strong ligands such as phosphines. To accelerate the hydrophosphination reaction, one of the chloro ligand in complex **3** was replaced with a labile ligand, acetonitrile, prior to the treatment with HPPH_2 (Scheme 2-6).

Scheme 2-6

The stable chloro ligand in complex **3** was initially removed quantitatively by treatment with AgPF_6 reagent to generate a vacant site which was then coordinated by one acetonitrile molecule in the solvent to form complex **6** (Scheme 2-6). This ligand exchange reaction was carried out in a mixed solvent system of dichloromethane and acetonitrile (1:2) at room temperature and was found to be complete in 1 day. After filtration through celite and the subsequent removal of solvent, complex **6** was obtained in 98% yield. Complex **6** is an air-stable brown solid that could be used directly for the further reactions without purification. In CDCl_3 , the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the coordinated phosphine complex **6** showed a singlet at δ -19.8. It is noteworthy that, unlike complex **3**, in CDCl_3 the two diastereotopic methyl groups of the alkyne moieties in complex **6** showed two doublet signals at δ 2.20 ($^4J_{\text{PH}} = 4.1$ Hz) and 2.25 ($^4J_{\text{PH}} = 4.1$ Hz) instead of one doublet signal in the ^1H NMR spectrum.

2.2.4 Hydrophosphination of dialkynylphosphine

The coordinated acetonitrile was replaced by HPPH_2 in dichloromethane at room temperature. This process was found to be complete in 1 day when monitored by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. After the coordination, in CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture showed a pair of doublets at δ -16.7 ($^2J_{\text{PP}} = 63.5$ Hz) and 36.1 ($^2J_{\text{PP}} = 63.5$ Hz), which indicated the formation of intermediate **7**. Subsequent addition of a trace amount of Et_3N to the reaction solution promoted the hydrophosphination reaction to give the product **8** in 3 h as a yellow solid in 47% yield (Scheme 2-7). In CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **8** showed a pair of doublets at δ 79.8 ($^3J_{\text{PP}} = 35.0$ Hz) and 28.8 ($^3J_{\text{PP}} = 35.0$ Hz). Yellow prisms were obtained after recrystallization of the product from dichloromethane and hexane.

Scheme 2-7

2.2.4.1 X-ray Structural Analysis of Complex **8**

The single crystal X-ray structure of complex **8** is shown in Figure 2-3. A pair of enantiomers exists with a ratio of 1:1 in each crystal unit cell. The cationic complex **8** exhibits the expected and usual "three-legged piano-stool" disposition with the benzene ligand occupying the "stool" position. The angles at the ruthenium center are in the range of 82.3(2)-88.5(2)°, which are unexceptional for (η^6 -arene)rutheniumchlorophosphine derivatives.^{307, 308} The newly generated diphosphine coordinates to ruthenium as a bidentate ligand via the two phosphorus atoms. The slightly shorter distance of Ru-P(2) [2.292(1) Å] than Ru-P(1) [2.320(1) Å] indicates that the Ru-P(2) bond is stronger, perhaps due to the less sterically demanding alkynyl group on P(2). Compared with the phenyl group on P(1), the less repulsion between the alkyne moiety on P(2) and the coordinated benzene allows the relatively short distance between P(2) and the ruthenium center, which is responsible for the shorter Ru-P(2) bond. At the stereogenic center, the alkynyl fragment on P(2) atom is distal to the Cl atom on ruthenium, which designates these two enantiomers as $S_P S_{Ru}$ and $R_P R_{Ru}$ configurations. Moreover, the C(19)-C(20) [1.506(3) Å] and C(20)-C(21) [1.336(3) Å] distances are typical for C-C and C=C bonds, respectively. Selected bond distances and angles for complex **8** are given in Table 2-3.

Figure 2-3 Molecular structure of complex 8

Table 2-3 Selected Bond Lengths (Å) and Angles (deg) of 8

Ru(1)-P(1)	2.320(1)	Ru(1)-P(2)	2.292(1)
Ru(1)-Cl(1)	2.400(1)	P(1)-C(7)	1.825(2)
P(1)-C(13)	1.834(2)	P(1)-C(20)	1.847(2)
P(2)-C(21)	1.806(2)	P(2)-C(22)	1.757(2)
P(2)-C(25)	1.818(2)	C(19)-C(20)	1.506(3)
C(20)-C(21)	1.336(3)		
P(1)-Ru(1)-P(2)	82.3(2)	P(1)-Ru(1)-Cl(1)	88.5(2)
P(2)-Ru(1)-Cl(1)	82.9(2)	C(7)-P(1)-Ru(1)	117.7(1)
C(13)-P(1)-Ru(1)	113.7(6)	C(20)-P(1)-Ru(1)	109.9(6)
C(7)-P(1)-C(13)	104.9(1)	C(7)-P(1)-C(20)	107.9(1)
C(13)-P(1)-C(20)	101.5(1)	C(21)-P(2)-Ru(1)	110.3(1)
C(22)-P(2)-Ru(1)	114.4(1)	C(25)-P(2)-Ru(1)	118.3(1)

C(21)-P(2)-C(25)	107.0(1)	C(21)-P(2)-C(22)	101.7(1)
C(22)-P(2)-C(25)	103.6(1)	C(19)-C(20)-P(1)	122.0(1)
C(21)-C(20)-P(1)	115.7(2)	C(19)-C(20)-C(21)	122.1(2)
C(20)-C(21)-P(2)	119.7 (2)		

2.2.4.2 Stereoselectivity of Hydrophosphination

This hydrophosphination reaction can theoretically produce two diastereomerically related pairs of enantiomers. The four isomers are designated, as shown in Scheme 2-8. During the hydrophosphination process, in CDCl_3 only one pair of doublet signals [δ 79.8 ($^3J_{\text{PP}} = 35.0$ Hz) and 28.8 ($^3J_{\text{PP}} = 35.0$ Hz)] in the ^{31}P NMR spectrum of the reaction mixture was observed, which indicated that only one diastereomer formed. The pair of signals (δ 79.8 and 28.8) observed in the crude product was in accordance with the signals in the ^{31}P NMR spectrum of the isolated product **8**. Thus it was deduced that this hydrophosphination generated the $S_{\text{P}}S_{\text{Ru}}$ and $R_{\text{P}}R_{\text{Ru}}$ racemates diastereoselectively.

The reason for the stereoselectivity is proposed to be related to the steric bulk of the HPPH_2 in the intermediate **7**. In the ^1H NMR spectrum of complex **3**, the NMR signals of the two methyl groups show up as one doublet signal at δ 2.12 ($^4J_{\text{PH}} = 3.8$ Hz), which indicates the two methyl groups are equivalent. In contrast, these two methyl groups exhibit two doublet signals at δ 2.20 ($^4J_{\text{PH}} = 4.1$ Hz) and 2.25 ($^4J_{\text{PH}} = 4.1$ Hz) in the ^1H NMR spectrum of complex **6**. Moreover, the ^1H NMR spectrum of the crude **7** also

shows two distinct doublet signals at δ 2.07 ($^4J_{\text{PH}} = 4.1$ Hz) and 2.13 ($^4J_{\text{PH}} = 4.1$ Hz), although the pure intermediate **7** could not be isolated. The difference in these spectra indicates that the two alkynyl groups in the coordinated $\text{PPh}(\text{C}\equiv\text{CCH}_3)_2$ moiety are located in distinct diastereotopic environments. Therefore the reaction takes place when the intermediate **7** adopts the sterically favored confirmation, which leads to the addition of the activated diphenylphosphine with good stereoselectivity.

Scheme 2-8

2.2.5 Insertion of Complex 8

The remaining unreacted alkyne moiety in complex **8** was observed to be

chemically reactive and could be inserted into the Pd-C bond of organopalladium complex **9**. The reaction was carried out in the presence of a 50% excess amount **9** at room temperature in dichloromethane and was found to be complete in 7 days when monitored using the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The crude mixture was then purified by silica gel column chromatography to give the bimetallic product **10** as a yellow solid in 25% yield (Scheme 2-9).

Scheme 2-9

2.2.5.1 Mechanistic Considerations

The suggested mechanism is shown in Scheme 2-10. The alkynyl group of complex **8** initially inserts into the Pd-C bond of complex **9** to form the intermediate **11**. A very important feature of the structure of complex **11** is the vacant site on the Pd atom; moreover, no free lone pair of electrons or ligands are available that can occupy this site. The palladium species with the vacant site then promotes the proton exchange process between the phenyl and the alkenyl group, which leads to the formation of complex **12**. After exchange, the agostic H (*ortho* to phosphorus) on the phenyl group is transferred to

the alkynyl group, forming a connection between phenyl group and palladium, which generates a C-olefin-N tridentate ligand. The subsequent coordination of C=C unit makes the tridentate ligand chelate to palladium, thus yielding the product **10**.

Scheme 2-10 (the square indicates the vacant coordination site)

2.2.5.2 Conformations of **10**

The complex **10** exists as two conformations, and the two corresponding compounds, **10a** and **10b**, as shown in Scheme 2-11 (PF_6^- is omitted for clarity), can be separated by silica gel column chromatography to give pure products as yellow solids with 22% (the major product, **10a**) and 3% (the minor product, **10b**) isolated yields, respectively. In CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **10a** contained a pair of doublets at δ 76.5 ($^3J_{\text{PP}} =$

32.8 Hz, PPh₂) and 47.5 [³J_{PP} = 32.8 Hz, P(C=C)₂]; while another pair of doublets at δ 75.5 (³J_{PP} = 27.7 Hz, PPh₂) and 64.3 [³J_{PP} = 27.7 Hz, P(C=C)₂] were observed in the ³¹P{¹H} NMR spectrum of **10b**. The ¹H and ¹³C{¹H} NMR spectra of complexes **10a** and **10b** have also been studied. In the ¹H NMR spectra of complexes **10a** and **10b** in CDCl₃, the coordinated benzene shows a singlet at δ 6.17 and 5.90, respectively, indicating the formation of two complexes. Moreover, In the ¹³C{¹H} NMR spectrum of complex **10a** in CDCl₃, the two newly generated alkenyl carbon atoms show two signals at δ 94.6 and 134.5. For complex **10b**, the corresponding alkenyl carbon atoms show similar signals at δ 95.4 and 134.5 in the ¹³C{¹H} NMR spectrum. However, these two alkenyl carbon atoms, which exists as two alkynyl carbon atoms in complex **8**, show two signals at δ 71.2 and 112.4 in the ¹³C{¹H} NMR spectrum of complex **8**. This ¹³C{¹H} NMR spectroscopy supports the fact that the alkynyl group in complex **8** has been converted into an alkene moiety in complex **10**. Recrystallization of **10a** from dichloromethane-diethyl ether gave brown prisms. The structure of **10b** was confirmed by 2D ROESY NMR studies. It is noteworthy that both diastereomers exist in their racemic forms.

Both **10a** and **10b** are stable in the solid state. However, in dichloromethane and in chloroform solution, slow interconversion takes place (Scheme 2-11). Attaining the chemical equilibrium requires 2 days, as revealed by the ³¹P{¹H} NMR analysis. On the basis of the integration in the ³¹P{¹H} NMR spectrum of the mixture, the ratio of **10a** to **10b** is 3:1 in the equilibrium state in chloroform; thus indicating that the conformation in **10a** is thermodynamically favored.

Scheme 2-11

The structures of the conformations in **10a** and **10b** are similar, as shown in Scheme 2-11. Each of them contains a tridentate ligand, which coordinates to palladium. The olefin C11-C12 coordinates to palladium, thus Pd, N20, C(19, 18, 13, 12) form a pseudo 6-membered ring. Because of the rigidities associated with the fragments, including the two aromatic rings, the olefin group C11-C12, the coordinated Pd moiety, and the angle of C11-P4-C5, the pseudo 6-membered ring adopts the stable boat conformation instead of the chair conformation. Changing the boat conformation into the chair conformation will lead to drastic distortions of those fragments. The parts below P4 in the structures of **10a** and **10b** are mirror-symmetrical, while the parts above P4 have the same configurations. The chiralities at ruthenium and P4 in the two compounds are

undoubtedly same because they are just compounds with different conformations of the same complex **10**. The mechanism of interconversion between **10a** and **10b** is not clear but this process should include the reversions of the pseudo 6-membered ring and the coordinative face of olefin C11-C12.

2.2.5.3 X-ray Structural Analysis of Compound **10a**

The single crystal X-ray structure of complex **10a** is shown in Figure 2-4. A pair of enantiomers exists with a ratio of 1:1 in each unit cell. The geometry at the ruthenium center exhibits the "three-legged piano-stool" disposition; the η^6 -coordinated arene is in a "stool" position while the "legs" comprise P and Cl atoms. The angles at the Ru center are in the range of 79.5(1)-87.4(1)°, which are unexceptional for (η^6 -arene)rutheniumphosphine derivatives.^{307, 308} The diphosphine coordinates to ruthenium as a bidentate ligand via the two phosphorus atoms. The bond lengths of Ru-P(1) and Ru-P(2) are 2.294(1) Å and 2.299(1) Å, respectively. The alkyne moiety in complex **8** has been converted into an C=C bond, C(28)-C(29), forming a new carbon-carbon bond, C(29)-C(31). The olefin, C(28)-C(29), coordinates to palladium, which leads to the short distances of Pd(1)-C(28) [2.123(3) Å] and Pd(1)-C(29) [2.322(3) Å]. Weakened by the coordination, the C=C bond length of 1.398(4) Å is slightly longer than the typical value. Furthermore, the P(1)Ph group connects to palladium through the *ortho* carbon-metal bond, C(27)-Pd(1), with a bond length of 2.011(3) Å. C(27), the olefin C(28)-C(29), and N(1) constitute a tridentate ligand that coordinates to the palladium center. Additionally, the absolute configuration at P(1)

remained unchanged, which was deduced from the fact that the olefin, C(28)-C(29), resulting from the conversion of the original alkyne, kept the distal position relative to the Cl atom on ruthenium. Selected bond distances and angles for complex **10a** are given in Table 2-4.

Figure 2-4 Molecular structure of compound **10a**

Table 2-4 Selected Bond Lengths (Å) and Angles (deg) of **10a**

Pd(1)-C(27)	2.011(3)	Pd(1)-C(28)	2.123(3)
Pd(1)-C(29)	2.322(3)	Pd(1)-N(1)	2.211(3)
Pd(1)-Cl(2)	2.321(1)	Ru(1)-P(1)	2.294(1)
Ru(1)-P(2)	2.299(1)	Ru(1)-Cl(1)	2.402(1)
P(1)-C(21)	1.811(3)	P(1)-C(22)	1.793(3)
P(1)-C(28)	1.828(3)	C(28)-C(29)	1.398(4)
C(29)-C(30)	1.520(4)	C(29)-C(31)	1.510(4)

C(27)-Pd(1)-C(28)	86.6(1)	C(27)-Pd(1)-C(29)	90.9(1)
C(27)-Pd(1)-N(1)	175.9(1)	C(27)-Pd(1)-Cl(2)	87.1(1)
C(28)-Pd(1)-C(29)	36.3(1)	C(28)-Pd(1)-N(1)	95.1(1)
C(28)-Pd(1)-Cl(2)	159.2(1)	C(29)-Pd(1)- N(1)	92.7(1)
C(29)-Pd(1)- Cl(2)	163.6(1)	N(1)-Pd(1)-Cl(2)	90.0(1)
P(1)-Ru(1)-P(2)	79.5(1)	P(1)-Ru(1)-Cl(1)	84.7(1)
P(2)-Ru(1)-Cl(1)	87.4(1)	C(21)-P(1)-C(22)	108.6(2)
C(21)-P(1)-C(28)	105.1(1)	C(21)-P(1)-Ru(1)	107.5(1)
C(22)-P(1)-C(28)	101.1(2)	C(22)-P(1)-Ru(1)	119.7(1)
C(28)-P(1)-Ru(1)	114.0(1)	P(1)-C(28)-Pd(1)	106.3(1)
P(1)-C(28)- C(29)	127.3(2)	C(29)-C(28)-Pd(1)	79.6(2)
C(28)-C(29)-C(30)	122.1(3)	C(28)-C(29)-C(31)	120.2(3)
C(28)-C(29)-Pd(1)	64.1(2)	C(30)-C(29)-C(31)	114.7(3)
C(30)-C(29)-Pd(1)	109.2(2)	C(31)-C(29)-Pd(1)	113.5(2)

2.2.5.4 2D ROESY Study of Compound 10b

Unfortunately, crystals of **10b** could not be obtained although various crystallization methods were attempted. However, the structure of **10b** has been studied through several experiments, including the 2D rotating frame nuclear Overhauser enhancement (ROESY) ¹H NMR technique. Scheme 2-11 shows the numbering Scheme of compound **10a** and

10b used in the 2D ROESY NMR analysis. Selected ^{31}P and ^1H NMR data of **10a** and **10b** are given in Table 2-5. These NMR assignments are based on a series of ^1H , ^{31}P , $^1\text{H}\{^{31}\text{P}\}$, and 2D ROESY NMR studies of these two compounds. Figures 2-5 and 2-6 show the 2D ^1H - ^1H ROESY NMR spectra of **10a** and **10b**, respectively.

The ^1H NMR spectra of **10a** and **10b** are similar. Their elemental analysis data are also in accordance with the calculated value. Furthermore, the LCMS (ESI) spectra of both compounds show a clear signal at 863, which is consistent with the signal of cation 10^+ . Therefore it is deduced that **10a** and **10b** have similar structures with the same molecular formulas. Through a Dreiding model study, the structure of **10b** is suggested as shown in Scheme 2-11. It is believed that several differences in the structures of **10a** and **10b** can be reflected in their 2D ROESY NMR spectra. In **10a**, two NMe groups and the H19(ax) are close to the coordinated benzene ligand on the Ru metal, while Me12 is far away. Contrastingly, in **10b**, those two corresponding NMe groups and H19(ax) are far away from the coordinated benzene ligand, while Me12 is close to it. Moreover, the distance between the coordinated benzene ligand and the H11 in **10a** is longer than in **10b**.

Figure 2-5. Two-dimensional ^1H ROESY NMR spectrum of complex **10a** in CDCl_3 . All off-diagonal peaks are of negative intensity except signal A. Selected NOE contacts: B, H19(eq)-Me20(ax); C, H19(eq)-Me20(eq); D, H19(ax)-Me20(eq); E, H19(ax)-H19(eq); F, H11-H19(ax); G, C_6H_6 -Me20(ax); H, C_6H_6 -Me20(eq); I, C_6H_6 -H19(ax); J, C_6H_6 -H11; K, H17-H19(eq); L, H17-Me20(ax); M, H3, Ph1-Me2; N, Ph1-Me12; O, Ph1-H11; PQ, Ph1- C_6H_6 ; R, Ph1-Me2; S, Me12-H14; T-W, signals of **10b**.

Figure 2-6. Two-dimensional ^1H ROESY NMR spectrum of complex **10b** in CDCl_3 . All off-diagonal peaks are of negative intensity except signal A. Selected NOE contacts: B, H19(eq)-Me20(ax); C, H19(eq)-Me20(eq); D, H19(ax)-Me20(eq); E, H19(ax)-H19(eq); F, H11-H19(ax); G, C_6H_6 -Me12; H, H17-H19(eq); I, H17-Me20(ax); JPQ, (H3, Ph1)-Me2; K, Ph1-H19(ax); L, Ph1-H11; M-N, Ph1- C_6H_6 ; O, Ph4- C_6H_6 ; R, Me12-H14.

Table 2-5. Selected ^{31}P and ^1H NMR Spectra Chemical Shift Values of **10a and **10b** in CDCl_3 (coupling constants in Hz are given in parentheses)**

	10a	10b
^{31}P	47.5 d ($^3J_{\text{PP}} = 32.8$) 76.5 d ($^3J_{\text{PP}} = 32.8$)	64.3 d ($^3J_{\text{PP}} = 27.7$) 75.5 d ($^3J_{\text{PP}} = 27.7$)
Me_2	2.03 ddd ($^3J_{\text{PH}} = 9.1$, $^4J_{\text{PH}} = ^4J_{\text{HH}} =$ 1.6)	2.22 ddd ($^3J_{\text{PH}} = 9.0$ $^4J_{\text{PH}} = ^4J_{\text{HH}} =$ 1.4)
Me_{12}	2.12 s	2.19 s
NMe(ax)	2.26 s	2.29 s
NMe(eq)	2.92 s	2.78 s
$\text{H}_{19(\text{eq})}$	3.41 d ($^2J_{\text{HH}} = 15.0$)	3.15 d ($^2J_{\text{HH}} = 14.0$)
$\text{H}_{19(\text{ax})}$	3.99 d ($^2J_{\text{HH}} = 15.0$)	4.02 d ($^2J_{\text{HH}} = 14.0$)
H_{11}	5.17 d ($^2J_{\text{PH}} = 20.9$)	5.40 d ($^2J_{\text{PH}} = 13.5$)
C_6H_6	6.17 s	5.90 s

Several similar interactions in **10a** and **10b** are found. The expected interactions within the benzylamine moiety are clearly shown in both spectra. The signals of

interactions between H19 and the NMe groups [B, H19(eq)-Me20(ax); C, H19(eq)-Me20(eq); D, H19(ax)-Me20(eq); no signal resulting from the interaction H19(ax)-Me20(ax)] are typical and clear in both the spectra. Additionally, other interactions have also been observed in both spectra. H19(eq) and Me20(ax) interact with the proton on the neighboring phenyl group (H17) [K, H17-H19(eq); L, H17-Me20(ax) in the case of **10a**; and H, H17-H19(eq); I, H17-Me20(ax) in the case of **10b**]. The interaction between Me12 and the nearby proton H14 on the neighboring phenyl group also takes place in each compound, which has been recorded as signal S in the case of **10a** and R in the case of **10b**. Moreover, H19(ax) interacts with H11 to give the strong signal F due to their extreme proximity.

The differences between the spectra of **10a** and **10b**, which are more important, are also clear. The 2D ROESY NMR spectrum of **10a** shows the interactions between the two NMe groups and the coordinated benzene ligand (G, H). The signal H is stronger than G since Me20(eq) is closer to the benzene group than Me20(ax). However, the corresponding signals have not been observed in the 2D ROESY spectrum of **10b**. Furthermore, in the case of **10a**, the coordinated benzene ligand also interacts with H19(ax) and H11 to give signals I and J, respectively, while the corresponding interactions are not found in the case of **10b**. In contrast, the 2D ROESY spectrum of **10a** does not show any signal due to the interaction between the coordinated benzene ligand and Me12, while the corresponding interaction has been recorded as a clear signal (G) in the 2D ROESY spectrum of **10b**. These differences between spectra of **10a** and **10b** indicate the different orientation of the coordinated benzene ligand in these two

complexes. In the case of **10a**, the coordinated benzene ligand is close to the NMe groups and far away from Me12. However, in the case of **10b**, the opposite scenario is evident.

In conclusion, these two spectra are in agreement with the interactions expected from the structures of the two compounds in Scheme 2-11; therefore the structure of **10b** is deduced. It should be noted that because the equilibrium exists, a small amount of **10b** was generated during the 2D ROESY experiment, which gave a few signals in the 2D ROESY NMR spectrum of **10a** (T-W).

2.2.6 Arene Displacement of Complexes 6 and 8

During the preparation of complexes **6** and **8**, by-products due to arene displacement by three acetonitrile molecules were observed. For (η^6 -benzene)ruthenium complexes, examples of arene displacement by three acetonitrile ligands are preceded.^{309, 310} This process is often promoted by heating or UV irradiation. However, some examples of arene displacement were also observed under mild conditions in the absence of photoirradiation.³⁰⁹ The mechanism proposed is generally based on the weakening of the metal-arene bond by heating, UV irradiation, or coordination of some ligands.

2.2.6.1 Arene Displacement of Complex 6

Arene displacement was not observed during the ligand exchange reaction. However,

the process of recrystallization in acetonitrile-diethyl ether led to the formation of complex **13** as yellow prisms, which indicated the arene displacement by three acetonitrile molecules, as shown in Scheme 2-12. It is noteworthy that the crystal of **6** was not formed during recrystallization in the above solvent system. In CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **13** showed a singlet at δ 14.2.

Scheme 2-12

The single crystal X-ray structure of complex **13** is shown in Figure 2-7. The geometry at ruthenium is an octahedral geometry with angles in the ranges of $88.5(1)$ - $88.5(2)^\circ$, and $177.6(1)$ - $177.8(1)^\circ$, respectively. Cl(1) occupies the *cis* position to P(1). The three Ru-N bond lengths *cis* to the phosphine ligand are significantly shorter [$2.018(2)$ Å- $2.022(2)$ Å] than the one *trans* to P(1) [Ru(1)-N(4), $2.121(2)$ Å]. However, for Ru(1)-N(3) *trans* to the Cl(1) atom, no such *trans*-effect is present, which is attributed to the lack of backbonding. Selected bond distances and angles for complex **3** are given in Table 2-6.

Figure 2-7 Molecular structure of complex **13**

Table 2-6 Selected Bond Lengths (Å) and Angles (deg) of **13**

Ru(1)-Cl(1)	2.400(1)	Ru(1)-N(1)	2.018(2)
Ru(1)-N(2)	2.022(2)	Ru(1)-N(3)	2.020(2)
Ru(1)-N(4)	2.121(2)	Ru(1)-P(1)	2.262(1)
P(1)-C(1)	1.815(2)	P(1)-C(7)	1.760(2)
P(1)-C(10)	1.756(2)	C(7)-C(8)	1.197(3)
C(10)-C(11)	1.189(3)		
P(1)-Ru(1)-Cl(1)	90.3(1)	P(1)-Ru(1)-N(1)	90.4(1)
P(1)-Ru(1)-N(2)	91.5(1)	P(1)-Ru(1)-N(3)	92.0(1)
P(1)-Ru(1)-N(4)	177.8(1)	Cl(1)-Ru(1)-N(1)	90.8(1)
Cl(1)-Ru(1)-N(2)	90.2(1)	Cl(1)-Ru(1)-N(3)	177.6(1)

Cl(1)-Ru(1)-N(4)	88.5(1)	N(1)-Ru(1)-N(2)	177.8(1)
N(1)-Ru(1)-N(3)	89.9(1)	N(1)-Ru(1)-N(4)	87.7(1)
N(2)-Ru(1)-N(3)	89.0(1)	N(2)-Ru(1)-N(4)	90.4(1)
N(3)-Ru(1)-N(4)	89.2(1)	Ru(1)-P(1)-C(1)	117.1(1)
Ru(1)-P(1)-C(7)	115.5(1)	Ru(1)-P(1)-C(10)	114.9(1)
C(1)-P(1)-C(7)	102.2(1)	C(1)-P(1)-C(10)	101.9(1)
C(7)-P(1)-C(10)	103.2(1)		

2.2.6.2 Arene Displacement of Complex **8**

When the coordination of diphenylphosphine was carried out in acetonitrile at room temperature, both the intermediate **7** and the by-product **14** were generated. This process was monitored by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy and was found to be complete very slowly. In CDCl_3 the signal for diphenylphosphine at δ -39.7 in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture disappeared after one week. On the integration of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, the amount of complex **14** in the reaction mixture was ca. 50%. After the reaction mixture was stirred for one more week, all the intermediate **7** was converted into the hydrophosphination product **8**, as revealed monitored by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Pure **14** was then isolated by silica gel column chromatography as a pale yellow solid in 30% yield. In CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **14** showed a pair of doublets at δ -6.7 ($^2J_{\text{PP}} = 393.0$ Hz) and 21.3 ($^2J_{\text{PP}} = 393.0$ Hz). Recrystallization of complex **14** from dichloromethane and diethyl ether gave pale yellow needles.

Scheme 2-13

The single crystal X-ray structure of complex **14** is shown in Figure 2-8. The geometry at ruthenium is an octahedron geometry with angles in the ranges of $87.5(2)$ – $93.5(3)^\circ$, and $176.7(4)$ – $178.9(1)^\circ$, respectively. Cl(1) occupies the *cis* position to P(1) and P(2). The two Ru–N bond lengths *cis* to Cl(1) are slightly shorter [$2.003(9)$ Å and $2.007(9)$ Å] than the one *trans* to Cl(1) [Ru(1)–N(2), $2.030(8)$ Å]. Additionally, the two Ru–P bond lengths [$2.353(3)$ Å and $2.348(3)$ Å] are also slightly longer than the corresponding Ru–P bond length in complex **13**, which is attributed to the *trans*-effect. Selected bond distances and angles for complex **3** are given in Table 2-7.

Figure 2-8 Molecular Structure of Complex 14

Table 2-7 Selected Bond Lengths (Å) and Angles (deg) of 14

Ru(1)-P(1)	2.353(3)	Ru(1)-P(2)	2.348(3)
Ru(1)-N(1)	2.003(9)	Ru(1)-N(2)	2.030(8)
Ru(1)-N(3)	2.007(9)	Ru(1)-Cl(1)	2.392(3)
P(1)-C(1)	1.837(10)	P(1)-C(7)	1.818(11)
P(2)-C(19)	1.755(13)	P(2)-C(22)	1.761(13)
P(2)-C(25)	1.791(13)	C(19)-C(20)	1.196(15)
C(22)-C(23)	1.176(17)		
P(1)-Ru(1)-P(2)	178.9(1)	P(1)-Ru(1)-N(1)	89.9(3)
P(1)-Ru(1)-N(2)	89.1(2)	P(1)-Ru(1)-N(3)	92.1(2)
P(1)-Ru(1)-Cl(1)	90.6(1)	P(2)-Ru(1)-N(1)	89.0(3)
P(2)-Ru(1)-N(2)	91.1(2)	P(2)-Ru(1)-N(3)	89.0(2)
P(2)-Ru(1)-Cl(1)	89.1(1)	N(1)-Ru(1)-N(2)	89.2(3)
N(1)-Ru(1)-N(3)	176.7(4)	N(1)-Ru(1)-Cl(1)	87.5(2)
N(2)-Ru(1)-N(3)	93.5(3)	N(2)-Ru(1)-Cl(1)	176.6(2)
N(3)-Ru(1)-Cl(1)	89.8(2)	Ru(1)-P(1)-C(1)	122.0(3)
Ru(1)-P(1)-C(7)	114.1(4)	C(1)-P(1)-C(7)	105.2(5)
Ru(1)-P(2)-C(19)	114.6(4)	Ru(1)-P(2)-C(22)	115.7(4)
Ru(1)-P(2)-C(25)	118.7(5)	C(19)-P(2)-C(22)	103.1(6)
C(19)-P(2)-C(25)	101.2(6)	C(22)-P(2)-C(25)	101.3(7)

2.3 Conclusions

Coordination of a dialkynylphosphine to the ruthenium center successfully induced the activation of the alkyne moieties. One of the two alkyne moieties underwent hydrophosphination with high diastereoselectivity. Two stereogenic centers at ruthenium and phosphorus were formed in the product during this process, but only one pair of enantiomers adopting $S_P S_{Ru}$ and $R_P R_{Ru}$ configurations have been observed and isolated after the reaction. Furthermore, the remaining unreacted alkyne moiety was subsequently functionalized through an insertion reaction. Insertion of the carbon-carbon triple bond into the Pd-C bond of cyclopalladated complex **9** generated a bimetallic product bearing a bifunctionalized phosphine. The configurations of the chiral ruthenium and phosphorus centers in the product were both retained after the insertion reaction. It is noteworthy that the bifunctionalized phosphine complex exists as two conformations, which can interconvert in solution. The two corresponding compounds for the two conformations were separated and identified by X-ray crystallographic and 2D ROESY NMR studies.

2.4 Experimental

Reactions involving air-sensitive compounds were performed under an inert atmosphere of argon using standard Schlenk techniques. Microdistillation was performed using a short path type of distilling head. NMR spectra were recorded at 25 °C on Bruker Avance 300, 400, and 500 spectrometers. Optical rotations were measured on the specified solution in a 0.1 dm cell at 25 °C with a Perkin-Elmer 341 polarimeter. Melting

points were determined on a SRS Optimelt automated melting point system, SRS MPA 100. Elemental analysis was performed by the Elemental Analysis Laboratory of the Division of Chemistry and Biological Chemistry at Nanyang Technological University. Mass spectra were recorded on an Finnigan LCQ Deca XP MAX mass spectrometer using the ES(+) or ES(-) techniques.

Prop-1-ynylidiphenylphosphine **4**³¹¹ and the dimeric benzylamine palladium(II) complex **9**³¹² were synthesized according to literature methods.

Synthesis of free phosphine ligand

Synthesis of diprop-1-ynylphenylphosphine, **1**

A solution of 1-propynylmagnesium bromide, BrMg-C≡CCH₃, (0.10 mol) in 300 mL THF was maintained at -78°C, and Cl₂PPh (8.95 g, 0.05 mol) was added dropwise slowly. The mixture was then allowed to recover to room temperature and stirred for 1.5 h, then refluxed for another 2.5 h. The resulting solution was cooled to room temperature and stirred for overnight. The solvent was removed through distillation, and the residue was neutralized with saturated NH₄Cl solution (ca. 200 mL) and extracted with diethyl ether (ca. 100 mL×3). The organic layer was separated, dried with MgSO₄, and then distilled to remove the solvent to give the crude product. Subsequent purification through microdistillation (102-104 °C/0.49 mmHg) gave pure phosphine **1** as a colorless liquid. Yield: 5.87 g (63%). ³¹P{¹H} NMR (CDCl₃, δ): -59.7 (s). ¹H NMR (CDCl₃, δ): 2.02 (d, ⁴J_{PH} = 1.7 Hz, 6H, PCC-Me); 7.38-7.44 (3H), 7.71-7.77 (2H) (m, P-Ph).

Coordination of phosphine ligands

Synthesis of (η^6 -Benzene)dichloro(phenyldi(prop-1-ynyl)phosphine)ruthenium, **3**

Solid [$(\eta^6$ -benzene)RuCl₂]₂ (0.70 g, 1.39 mmol) was added into the solution of PPh(C $\equiv$ CCH₃)₂ (0.52 g, 2.79 mmol) in acetone (30 mL), and this reddish-brown suspension was stirred for 1 day. The resulting reddish-orange suspension was then evaporated to dryness. The orange solid was washed with hexane (ca. 30 mL) and dried *in vacuo* to give the product **3**. Yield: 1.18 g (97%). This solid was pure according to the NMR analysis and could be directly used for next reactions without further purification. Recrystallization of **3** from chloroform and diethyl ether gave red needles. MS ES (+): *m/z* 895 [2M+Na]⁺ 100%; 459 [M+Na]⁺ 50%. Mp: 220-222 °C dec. ³¹P{¹H} NMR (CDCl₃, δ): -20.2 (s). ¹H NMR (CDCl₃, δ): 2.12 (d, ⁴*J*_{PH} = 3.8 Hz, 6H, PCC-Me); 5.54 (d, ³*J*_{PH} = 1.0 Hz, 6H, C₆H₆); 7.43-7.46 (3H), 8.02-8.10 (2H) (m, P-Ph). Anal. Calcd for C₁₈H₁₇Cl₂PRu: C, 49.6; H, 3.9. Found: C, 50.0; H, 3.9.

Synthesis of (η^6 -Benzene)dichloro(diphenyl(prop-1-ynyl)phosphine)ruthenium, **5**

Solid [$(\eta^6$ -benzene)RuCl₂]₂ (0.24 g, 0.49 mmol) was added into the solution of PPh₂(C $\equiv$ CCH₃) (0.22 g, 0.97 mmol) in acetone (10 mL), and this reddish-brown suspension was stirred overnight. The resulting reddish-orange suspension was then evaporated to dryness. The orange solid was washed with a small amount of hexane and dried *in vacuo* to give **5**. Yield: 0.45 g (98%). This solid was pure according to the NMR analysis and could be directly used for next reactions without further purification. Recrystallization of **5** from dichloromethane and diethyl ether gave red needles. HRMS EI: *m/z* calculated for C₂₁H₁₉Cl₂PRu [M]⁺: 473.9645. Found: 473.9654. Mp: 220-222 °C

dec. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 0.1 (s). ^1H NMR (CDCl_3 , δ): 2.26 (d, $^4J_{\text{PH}} = 3.5$ Hz, 3H, PCC-Me); 5.56 (d, $^3J_{\text{PH}} = 0.9$ Hz, 6H, C_6H_6); 7.33-7.43 (6H), 7.90-7.98 (4H) (m, P-Ph).
 Anal. Calcd for $\text{C}_{21}\text{H}_{19}\text{Cl}_2\text{PRu}$: C, 53.2; H, 4.0. Found: C, 53.1; H, 3.8.

Hydrophosphination Reaction

Synthesis of 6

The solution of **3** (0.54 g, 1.24 mmol) in dichloromethane (120 mL) was mixed with the solution of AgPF_6 (0.31 g, 1.24 mmol) in acetonitrile (240 mL) and stirred in the absence of light for 1 day. Then the yellow suspension was filtered through Celite to remove AgCl . The yellow filtrate was evaporated and dried *in vacuo* to give **6** as a brown solid. Yield: 0.71 g (98%). This solid was pure according to the NMR analysis and could be directly used for next reactions without further purification. MS ES (+): m/z 442 $[\text{M-PF}_6]^+$ 100%; 401 $[\text{M-PF}_6\text{-NCMe}]^+$ 40%. Mp: 116-119 °C. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ): -143.7 (sept, PF_6^-); -19.8 (s). ^1H NMR (CDCl_3 , δ): 2.19 (s, 3H, NCMe); 2.20 (3H), 2.25 (3H) (d, $^4J_{\text{PH}} = 4.1$ Hz, PCC-Me); 5.91 (d, $^3J_{\text{PH}} = 1.1$ Hz, 6H, C_6H_6); 7.46-7.51 (3H), 7.84-7.92 (2H) (m, P-Ph). Anal. Calcd for $\text{C}_{20}\text{H}_{20}\text{ClF}_6\text{NP}_2\text{Ru}\cdot 0.5\text{CH}_2\text{Cl}_2$: C, 39.1; H, 3.4; N, 2.2. Found: C, 39.5; H, 3.6; N, 2.4.

Synthesis of 8

A solution of HPPH_2 (0.041 g, 0.22 mmol) in dichloromethane (20 mL) was stirred with **6** (0.13 g, 0.22 mmol) for 1 day to generate the intermediate **7** *in situ*. Then a trace amount of Et_3N (ca. 0.005 g, 0.049 mmol) was added and stirred for further 3 h until the ^{31}P NMR spectrum of reaction mixture indicated the conversion was completed. Removal

of the solvent gave the crude hydrophosphination product as a dark residue. Subsequent purification of the crude product by silica gel column chromatography (acetone-dichloromethane, 1:25) gave pure **8** as a yellow solid. Yield: 0.076 g (47%). The product was recrystallized from dichloromethane-hexane as yellow prisms, which were suitable for X-ray analysis. MS ES (+): m/z 587 $[M-PF_6]^+$. Mp: 260-262 °C dec. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): -143.6 (sept, PF_6^-); 28.8 (d, $^3J_{PP} = 35.0$ Hz, 1P); 79.8 (d, $^3J_{PP} = 35.0$ Hz, 1P). 1H NMR ($CDCl_3$, δ): 2.18 (ddd, $^3J_{PH} = 8.4$ Hz, $^4J_{PH} = ^4J_{HH} = 1.6$ Hz, 3H, C=C-Me); 2.25 (d, $^4J_{PH} = 3.8$ Hz, 3H, PCC-Me); 5.79 (s, 6H, C_6H_6); 6.88 (ddq, $^2J_{PH} = 52.9$ Hz, $^3J_{PH} = 12.7$ Hz, $^4J_{HH} = 1.4$ Hz, 1H, C=C-H); 7.39-7.92 (m, 15H, aromatics). Anal. Calcd for $C_{30}H_{28}ClF_6P_3Ru$: C, 49.2; H, 3.9. Found: C, 49.4; H, 3.9.

Insertion Reaction

Synthesis of **10**

To a solution of **8** (0.13 g, 0.18 mmol) in dichloromethane (15 mL) was added solid **9** (0.075 g, 0.14 mmol) in portions over 4 days. The resulting mixture was stirred for a further 3 days. The resulting dark yellow solution was concentrated and purified by silica gel column chromatography (acetone-dichloromethane, 1:25) to give pure **10a** and **10b** both as yellow solids. Yield: **10a**, 0.040 g (22%); **10b**, 0.006 g (3%). Complex **10a** was recrystallized from dichloromethane-diethyl ether as brown prisms, which were suitable for X-ray analysis. For **10a**: MS ES (+): m/z 863 $[M-PF_6]^+$. Mp: 210-212 °C dec. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): -143.8 (sept, PF_6^-); 47.5 (d, $^3J_{PP} = 32.8$ Hz, 1P); 76.5 (d, $^3J_{PP} = 32.8$ Hz, 1P). 1H NMR ($CDCl_3$, δ): 2.03 (ddd, $^3J_{PH} = 9.1$ Hz, $^4J_{PH} = ^4J_{HH} = 1.6$ Hz, 3H, Me_2); 2.12 (s, 3H, Me_{12}); 2.26 (s, 3H, NMe_{ax}); 2.92 (s, 3H, NMe_{eq}); 3.41 (d, $^2J_{HH} = 15.0$ Hz, 1H,

$H_{19,eq}$); 3.99 (d, $^2J_{HH} = 15.0$ Hz, 1H, $H_{19,ax}$); 5.17 (d, $^2J_{PH} = 20.9$ Hz, 1H, H_{11}); 6.17 (s, 6H, C_6H_6); 6.90-7.97 (m, 19H, H_3 and aromatics). Anal. Calcd for $C_{39}H_{40}Cl_2F_6NP_3PdRu \cdot CH_2Cl_2$: C, 44.0; H, 3.9; N, 1.3. Found: C, 44.2; H, 4.0; N, 1.7. For **10b**: MS ES (+): m/z 863 $[M-PF_6]^+$ 30%; 828 $[M-PF_6-Cl]^+$ 100%. Mp: 225-227 °C dec. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): -143.9 (sept, PF_6^-); 64.3 (d, $^3J_{PP} = 27.7$ Hz, 1P); 75.5 (d, $^3J_{PP} = 27.7$ Hz, 1P). 1H NMR ($CDCl_3$, δ): 2.19 (s, 3H, Me_{12}); 2.22 (ddd, $^3J_{PH} = 9.0$ Hz, $^4J_{PH} = 4J_{HH} = 1.4$ Hz, 3H, Me_2); 2.29 (s, 3H, NMe_{ax}); 2.78 (s, 3H, NMe_{eq}); 3.15 (d, $^2J_{HH} = 14.0$ Hz, 1H, $H_{19,eq}$); 4.02 (d, $^2J_{HH} = 14.0$ Hz, 1H, $H_{19,ax}$); 5.40 (d, $^2J_{PH} = 13.5$ Hz, 1H, H_{11}); 5.90 (s, 6H, C_6H_6); 7.16-8.12 (m, 19H, H_3 and aromatics). Anal. Calcd for $C_{39}H_{40}Cl_2F_6NP_3PdRu \cdot CH_2Cl_2$: C, 44.0; H, 3.9; N, 1.3. Found: C, 44.4; H, 4.3; N, 1.5.

Arene Displacement Studies

Synthesis of 13

Recrystallization of **6** from acetonitrile and diethyl ether gave **13** as yellow prisms. MS ES (+): m/z 487 $[M-PF_6]^+$ 100%; 446 $[M-PF_6-NMe]^+$ 50%. Mp: 200 °C dec. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): -142.5 (sept, PF_6^-); 14.2 (s). 1H NMR ($CDCl_3$, δ): 2.09-2.15 (9H), 2.27-2.30 (9H) (m, NMe + $PCC-Me$); 7.49-7.52 (3H), 7.83-7.91 (2H) (m, $P-Ph$). Anal. Calcd for $C_{20}H_{23}ClF_6N_4P_2Ru \cdot CH_2Cl_2$: C, 35.2; H, 3.5; N, 7.8. Found: C, 35.3; H, 3.4; N, 7.1.

Synthesis of 14

A solution of $HPPh_2$ (0.080 g, 0.43 mmol) in acetonitrile (20 mL) was stirred with the solution of **2** (0.25 g, 0.42 mmol) in acetonitrile (15 mL) for 1 week when ^{31}P NMR

spectrum of the reaction mixture showed no HPPH_2 existed. The mixture was then stirred for further 1 week. The resulting solution was concentrated and purified by silica gel column chromatography (acetone-dichloromethane, 1:25) to give pure **8** as a yellow solid and **14** as a pale yellow solid. Yield: **8**, 0.094 g (30%); **14**, 0.079 g (30%). The product **14** was recrystallized from dichloromethane-diethyl ether as pale yellow needles, which were suitable for X-ray analysis. For **14**: Mp: 183-185 °C dec. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ) (162 MHz): -144.0 (sept, PF_6^-); -6.7 (d, $^2J_{\text{PP}} = 393.0$ Hz, 1P); 21.3(d, $^3J_{\text{PP}} = 393.0$ Hz, 1P). ^1H NMR (CDCl_3 , δ) (400 MHz): 1.87 (6H), 2.38 (3H) (s, NCMe); 2.15 (d, $^4J_{\text{PH}} = 2.8$ Hz, 3H, PCC-Me); 6.09 (d, $^1J_{\text{PH}} = 12.7$ Hz, 1H, P-H); 7.43-7.93 (m, 15H, aromatics). Anal. Calcd for $\text{C}_{30}\text{H}_{31}\text{ClF}_6\text{N}_3\text{P}_3\text{Ru}\cdot\text{Et}_2\text{O}$: C, 48.0; H, 4.9; N, 4.9. Found: C, 47.6; H, 4.9; N, 5.0.

Chapter 3

Ruthenium Promoted Insertion of Dialkynylphosphine into Pd-C bond of Cyclopalladated Complex

3.1 Introduction

For many years, the facile insertion of carbon-carbon triple bonds into Pd-C bonds was regarded as an important step involved in organic reactions for the syntheses of both poly and heterocyclic compounds.^{302, 313} The isolatable organometallic complexes resulting from the insertion of alkynes into a Pd-C bond have often been shown to be genuine intermediates in the formation of the organic products.³⁰³ In most cases, the carbon in a Pd-C bond is aromatic; while insertion reactions into a palladium-alkyl carbon bond were also reported.

Palladacycles, which were often prepared directly by cleavage of a C-H bond close to a suitable donor atom,^{314, 315} are frequently used in insertion reactions. The reported palladacycles include those palladium(II) complexes containing biphenyl group;³¹⁶ orthopalladated primary benzylamine³¹⁷, secondary amine,^{318, 319} N-benzylidenaniline derivatives³²⁰; naphthalene complexes,³¹³ and other complexes (Scheme 3-1).^{303, 313,}

321-323

Scheme 3-1

Under very mild conditions, various alkynes were found to insert into the Pd-C bond of cyclopalladated complexes, particularly, those involving tertiary benzylamines, to give "singly inserted" or "doubly inserted" compounds, depending on the nature of alkynes involved (Scheme 3-2). A kinetic study has shown that prior to the rate-limiting insertion into the Pd-C bond of halo-bridged palladacycles, alkynes coordinated to Pd(II) via a bridge-opening route.³⁰⁵ Both electronic and steric effects have been invoked to explain the regioselectivities observed in those insertion reactions. However, although the latter argument is generally preferred, neither could be satisfactory in all cases.³⁰²⁻³⁰⁴

$R/X = 4\text{-MeO/Cl}, 5\text{-Me/Cl}, \text{H/Cl}, 5\text{-F/Cl}, \text{H/I}$

$R'/R'' = \text{Ph/Ph}, \text{Ph/C}_6\text{H}_4\text{NO}_2\text{-4}, \text{Ph/C}_6\text{H}_4\text{CF}_3\text{-3}, \text{Et/Et}$

Scheme 3-2

Scheme 3-3

Recently, our group studied the insertion reactions of alkynylphosphine complexes with cyclopalladated complexes involving benzylamines.³⁰⁶ Coordination of the alkynylphosphines to the palladium or platinum center successfully induced the activation of the alkyne moiety, which sequentially underwent insertions into the Pd-C bonds of cyclopalladated complexes with high reactivities (Scheme 3-3). In this project,

insertion reactions promoted by the coordination of alkynylphosphine to ruthenium are investigated.

3.2 Results and Discussion

3.2.1 Insertion Reaction of Monoalkynylphosphine Complex **5** and Chiral Palladium Dimer **15**, Synthesis of Complex **16**

Activated by the coordination of the alkynylphosphine to the ruthenium center, complex **5** underwent the insertion reaction with 0.5 equiv of organopalladium dimer **15** to give the product **16**. When monitored by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, this reaction was found to be complete in 2 days at room temperature in dichloromethane. After insertion, in CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture exhibited 2 singlet signals at δ 60.0 and 13.0 with a ratio of 4:1. The signal at δ 60.0 indicated the formation of the desired insertion product **16**; while the signal at δ 13.0 was assigned to the unexpected bimetallic palladium(II) product **17** (Scheme 3-4).

The crude mixture was purified by silica gel column chromatography and the eluted fractions were then precipitated by diethyl ether to give **16** as an orange solid in 51% yield and **17** as a yellow solid in 10% yield, respectively. Recrystallization of complex **16** from dichloromethane and diethyl ether gave red prisms. In CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **16** showed a singlet at δ 60.0. For complex **17**, yellow prisms were obtained by recrystallization from dichloromethane and diethyl ether. In CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR

spectrum of **17** showed a singlet at δ 13.0. It should be noted that complex **17** has been synthesized through another method by our group.³⁰⁶

Scheme 3-4

3.2.1.1 X-ray Structural Analysis of Complex 16

The single crystal X-ray structure of complex **16** is shown in Figure 3-1. The geometry at ruthenium exhibits the "three-legged piano-stool" disposition; the η^6 -coordinated arene is in a "stool" position while the "legs" comprise P and Cl atoms. The angles at the Ru center are in the range of 83.8(1)-87.7(1) $^\circ$, which are unexceptional for (η^6 -arene)rutheniumchlorophospine derivatives.^{307, 308} Furthermore, the geometry at palladium is a slightly distorted square planar with bond angles in the ranges of 85.0(1)-97.1(1) $^\circ$ and 171.0(1)-174.7(1) $^\circ$, respectively. As expected, the chloride bridge has been formed in the molecule. The bond lengths of Ru(1)-Cl(1) and Pd(1)-Cl(1) are 2.409(1) Å and 2.352(1) Å, respectively, and the angle of Ru(1)-Cl(1)-Pd(1) is 114.2(1) $^\circ$.

The unsaturated alkyne moiety of the alkynylphosphine has been inserted into the Pd-C bond of complex **15**, forming a new carbon-carbon bond between C(1) and C(12) and a new metal-carbon bond between Pd(1) and C(13). Furthermore, the absolute configuration at C(7) remained unchanged. Selected bond distances and angles for complex **16** are given in Table 3-1.

Figure 3-1 Molecular structure of complex **16**

Table 3-1 Selected Bond Lengths (Å) and Angles (deg) of **16**

Ru(1)-P(1)	2.333(1)	Ru(1)-Cl(1)	2.409(1)
Ru(1)-Cl(2)	2.407(1)	Pd(1)-Cl(1)	2.352(1)
Pd(1)-Cl(3)	2.419 (1)	Pd(1)-N(1)	2.140(2)
Pd(1)-C(13)	1.995(2)	P(1)-C(13)	1.815(2)
P(1)-C(14)	1.816(2)	P(1)-C(20)	1.837(2)
C(12)-C(13)	1.351(3)		

P(1)-Ru(1)-Cl(1)	83.8(1)	P(1)-Ru(1)-Cl(2)	86.3(1)
Cl(1)-Ru(1)-Cl(2)	87.7(1)	Cl(1)-Pd(1)-Cl(3)	85.0(1)
Cl(3)-Pd(1)-N(1)	97.1(1)	N(1)-Pd(1)-C(13)	91.6(1)
C(13)-Pd(1)-Cl(1)	86.5(1)	Cl(1)-Pd(1)-N(1)	174.7(1)
Cl(3)-Pd(1)-C(13)	171.0(1)	C(13)-P(1)-C(14)	107.7(1)
C(14)-P(1)-Ru(1)	117.5(1)	Ru(1)-P(1)-C(20)	108.4(1)
C(20)-P(1)-C(13)	107.3(1)	C(13)-P(1)-Ru(1)	110.9(1)
C(14)-P(1)-C(20)	104.5(1)	Ru(1)-Cl(1)-Pd(1)	114.2(1)

3.2.1.2 Absolute Configuration at Ruthenium in Complex **16**

It is noteworthy that complex **16** resulting from the insertion process contains a stereogenic center at ruthenium. The formation of the chirality of ruthenium has been attributed to the formation of the chloride bridge, which makes the two chlorine atoms non-equivalent. Complex **16** is optically pure in the solid state since only one isomer has been found in each unit cell. The solution of complex **16** in CHCl₃ also shows optical purity $\{[\alpha]_D +332.0^\circ (c\ 0.5, \text{CHCl}_3)\}$ and in CDCl₃ the ¹H NMR spectrum shows only one set of signals.

Since the optically pure crystals and stable spectroscopic data in solution were observed, the configuration at ruthenium in complex **16** is believed to be

thermodynamically stable. Furthermore, it is also deduced that the chirality at ruthenium is affected by the chiral carbon neighboring the NMe₂ group of complex **15**, which is the sole asymmetric factor in all reactants, as illustrated in Scheme 3-5 (the circle around the P atom represents the Ru atom). The structure shown as Scheme 3-5a is in accordance with the X-ray structure of complex **16**, while the structures shown as b-d are the other three possible structures. Since C7 adopts the *S* absolute configuration, Me8 occupies the equatorial position in Scheme 3-5a and b, while it is in the axial position in Scheme 3-5c and d. It is clear that the axial Me8 leads to the generation of the repulsion between Me8 and Me11, which indicates that the corresponding structures (Scheme 3-5c and d) are sterically unfavored. On the other hand, the steric factors resulting from the substituents on phosphorus and ruthenium are also critical for the formation of the favored configuration at ruthenium. The coordinative Cl-Pd bond is generally regarded as a weak bond, therefore the palladium atom could leave from the μ -chlorine readily and then connect with the other free chlorine to form a new chloride bridge, which converts the structures in Scheme 3-5a and c into the structures in Scheme 3-5b and d, respectively, or vice versa. It is noteworthy that the angle, Cl-Ru-Cl, is about 90° since the geometry at ruthenium is octahedral rather than tetrahedral. This angle leads to the 90° rotation of the Ru-P bond during the interconversion between the structures in Scheme 3-5a, c and those in Scheme 3-5b, d, which results in the proximity between the phenyl group and the free chlorine atom in the structures of Scheme 3-5b, d and thus generates the repulsion between them. To sum up the above arguments, there are no clear repulsions supported by the model studies in the structure shown in Scheme 3-5a, which indicates that it is the thermodynamically stable configuration of complex **16**.

Scheme 3-5

3.2.1.3 Mechanistic Considerations on the Formation of **17**

The insertion reaction of complexes **5** and **15** leads to the formation of the unexpected homobimetallic palladium(II) complex **17** as well as the desired heterobimetallic ruthenium(II)-palladium(II) product **16**. Complex **17** is believed to be generated through the reaction of the cyclopalladated dimer **15** and the organopalladium complex **18**, which contained an alkynylphosphine and was generated through a ligand exchange process between complex **5** with **15** (Scheme 3-6). During the reaction of complexes **5** and **15**, in CDCl_3 a singlet at δ 12.6 was observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture, indicating the formation of intermediate **18**.

Scheme 3-6

It is noteworthy that the insertion reaction of the cyclopalladated dimer **15** and complex **18** has been described in our group's previous work.³⁰⁶ In this earlier report, the insertion reaction was completed in 8 h at room temperature in dichloromethane.

3.2.1.4 Ligand Exchange between Ru and Pd Reactants

The formation of complex **17** indicates that there is a ligand exchange reaction in the reaction of complex **5** and **15**. The suggested mechanism is shown in Scheme 3-6. As a consequence of this ligand exchange reaction, two kinds of P-coordinated alkynylphosphine complexes, the ruthenium and palladium complexes, coexist in the solution during the reaction. The insertion reaction of the ruthenium complex **5** gives the heterobimetallic ruthenium(II)-palladium(II) product **16**, while the insertion reaction of the palladium complex **18** generates the homobimetallic palladium(II) complex **17**.

The reverse ligand exchange reaction has also been evidenced by the reaction of the (η^6 -benzene)ruthenium dimer **2** and the organopalladium complex **18**, as shown in Scheme 3-7. After this reaction, complex **16**, **17**, and **5** were isolated in 11%, 32%, and 15% yields, respectively. The organopalladium dimer **15** is clearly formed through the ligand exchange reaction shown in Scheme 3-6. Furthermore, the ruthenium complex **5** was also generated in the reaction of complex **2** and **18**, which further supports this ligand exchange process.

Scheme 3-7

3.2.2 Insertion Reaction of Monoalkynylphosphine Complex **5** and Nonchiral Palladium Dimer **9**, Synthesis of Complex **19**

The insertion of the alkyne moiety of complex **5** into the Pd-C bond in the nonchiral palladacycle **9** has also been studied. Activated by the coordination of the alkynylphosphine to the ruthenium center, complex **5** underwent the insertion reaction

with 0.5 equiv of organopalladium dimer **9** to give the product **19**. When monitored by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, this reaction was found to be complete in 2 days at room temperature in dichloromethane. After insertion, in CDCl_3 , the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture exhibited 2 singlet signals at δ 60.0 and 15.0 in a ratio of 10:1. The signal at δ 60.0 indicated that the formation of the desired insertion product **19**, while the signal at δ 15.0 was assigned to the by-product bimetallic palladium(II) **20** (Scheme 3-8).

Scheme 3-8

The crude mixture was purified by silica gel column chromatography and the eluted fractions were then precipitated by diethyl ether to give **19** as an orange solid in 65% yield and **20** as a yellow solid in 4% yield, respectively. Attempts at recrystallization of complex **19** from various solvent systems failed to give the corresponding crystals, while recrystallization of complex **20** from dichloromethane and diethyl ether generated yellow prisms. In CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complexes **19** and **20** showed singlets at

δ 60.0 and 15.0, respectively.

3.2.2.1 Ligand Exchange between Ru and Pd Reactants

There is also a ligand exchange process between complexes **5** and **9** since the by-product **20** was observed in the reaction mixture. The suggested mechanism of the reaction of **5** and **9** is similar to that of the reaction involving chiral organopalladium dimer **15** (Scheme 3-6). The insertion reaction of the ruthenium complex **5** gives the heterobimetallic ruthenium(II)-palladium(II) product **19**, while the insertion reaction of the palladium complex **21** bearing a coordinated alkynylphosphine (Scheme 3-9) generates the homobimetallic palladium(II) complex **20**.

The reverse ligand exchange reaction has also been studied through the reaction of the (η^6 -benzene)ruthenium dimer **2** and the organopalladium complex **21**, as shown in Scheme 3-9. After the reaction, complex **19**, **20**, and **5** were isolated in 35%, 19%, and 14% yields, respectively. The organopalladium dimer **9** is clearly formed through the ligand exchange reaction between complexes **2** and **21**. Furthermore, the ruthenium complex **5** was also generated in the reaction of complex **2** and **21**, which is another evidence for the above mentioned ligand exchange process.

Scheme 3-9

3.2.2.2 X-ray Structural Analysis of Complex **20**

The result of the single crystal X-ray structure determination of complex **20** is shown in Figure 3-1. The geometry at palladium center is a slightly distorted square planar with bond angles at Pd(1) in the ranges of $81.6(1)$ - $96.6(1)^\circ$ and $174.3(1)$ - $177.5(1)^\circ$, while those at Pd(2) range from $84.0(1)$ - $94.5(1)^\circ$ and $166.7(1)$ - $170.2(1)^\circ$, respectively. A chloride bridge has been formed in the molecule after insertion. The bond lengths of Pd(1)-Cl(1) and Pd(2)-Cl(1) are $2.427(1)$ Å and $2.352(1)$ Å, respectively; and the angle of Pd(1)-Cl(1)-Pd(2) is $84.8(1)^\circ$, which is smaller than the corresponding angle, Pd(1)-Cl(1)-Ru(1) [$114.2(1)^\circ$], in complex **16**. The unsaturated alkyne moiety of the alkynylphosphine has been inserted into the Pd-C bond of the cyclopalladated complex **9**, forming a new carbon-carbon bond between C(23) and C(25) and a new metal-carbon bond between Pd(2) and C(22). Selected bond distances and angles for complex **20** are given in Table 3-2.

Figure 3-2 Molecular structure of complex **20**

Table 3-2 Selected Bond Lengths (Å) and Angles (deg) of **20**

Pd(1)-P(1)	2.253(1)	Pd(1)-Cl(1)	2.427(1)
Pd(1)-N(1)	2.147(2)	Pd(1)-C(1)	2.001(3)
Pd(2)-Cl(1)	2.353 (1)	Pd(2)-Cl(2)	2.439(1)
Pd(2)-N(2)	2.104(2)	Pd(2)-C(22)	1.991(2)
P(1)-C(10)	1.821(2)	P(1)-C(16)	1.819(2)
P(1)-C(22)	1.812(2)	C(22)-C(23)	1.338(3)
P(1)-Pd(1)-Cl(1)	87.6(1)	P(1)-Pd(1)-N(1)	177.5(1)
P(1)-Pd(1)-C(1)	96.6(1)	Cl(1)-Pd(1)-N(1)	94.1(1)
Cl(1)-Pd(1)-C(1)	174.3(1)	N(1)-Pd(1)-C(1)	81.6(1)
Cl(1)-Pd(2)-Cl(2)	88.9(1)	Cl(1)-Pd(2)-N(2)	170.2(1)
Cl(1)-Pd(2)-C(22)	84.0(1)	Cl(2)-Pd(2)-N(2)	94.5(1)

Cl(2)-Pd(2)-C(22)	166.7(1)	N(2)-Pd(2)-C(22)	94.3(1)
Pd(1)-P(1)-C(10)	108.6(1)	Pd(1)-P(1)-C(16)	119.6(1)
Pd(1)-P(1)-C(22)	109.3(1)	C(10)-P(1)-C(16)	108.1(1)
C(10)-P(1)-C(22)	111.1(1)	C(16)-P(1)-C(22)	99.9(1)
Pd(1)-Cl(1)-Pd(2)	84.8(1)		

3.2.2.3 Comparison of Reactions Involving Chiral and Nonchiral Cyclopalladated Complexes

The yield of the heterobimetallic ruthenium-palladium complex **19** (65% in Scheme 3-8 and 35% in Scheme 3-9, respectively) in the insertions involving the nonchiral cyclopalladated complexes is significantly higher than the yield of the corresponding heterobimetallic complex **16** (51% in Scheme 3-4 and 11% in Scheme 3-7, respectively) in the reactions involving the chiral cyclopalladated complexes, irrespective of whether the reaction proceeds through the pathway from the ruthenium complex bearing a coordinated alkynylphosphine and the cyclopalladated dimer (Scheme 3-4 and 3-8) or the palladium complex bearing a coordinated alkynylphosphine and the (η^6 -benzene)ruthenium dimer (Scheme 3-7 and 3-9). However, for the yields of the homobimetallic palladium complex, the result is contrary. The possible reason is that the insertion rate of the chiral complex **18** into the Pd-C bond of palladacycle is much higher than that of the nonchiral complex **21**. The former reaction was found to be complete in 8 h at room temperature in dichloromethane in quantitative yield (Scheme 3-10a), while

the latter was found to be complete in 6 days under the same condition in quantitative yield (Scheme 3-10b). The low rate in the reaction of nonchiral complexes **9** and **21** leads to the generation of complex **19** in relative high yield in the corresponding reactions (Scheme 3-8 and 3-9) due to the kinetic reaction control, while in the reactions involving chiral complexes (Scheme 3-4 and 3-7), the relative low yield of complex **16** was obtained.

Scheme 3-10

3.2.3 Insertion Reaction of Dialkynylphosphine Complex **3** and Chiral Palladium Dimer **15**, Synthesis of Complex **22**

Insertion of one alkyne moiety of an activated dialkynylphosphine into the Pd-C bond of cyclopalladated complexes involving benzylamines generated a stereogenic center at phosphorus successfully. Activated by the coordination of the dialkynylphosphine to the ruthenium center, complex **3** underwent the insertion reaction

with 0.5 equiv of organopalladium dimer **15** to give the product **22**. When monitored by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, this reaction was found to be complete in 1 day at room temperature in dichloromethane. After the insertion, in CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture exhibited 2 singlets at δ 11.5 and 22.8 in a ratio of 1:1.1, which indicated two diastereoisomers being formed (Scheme 3-11). The homobimetallic palladium complex similar to complex **17** has not been observed.

Scheme 3-11

The crude mixture was purified by silica gel column chromatography and the eluted fractions were precipitated by diethyl ether to give $(R_{\text{Ru}}R_{\text{P}}S_{\text{C}})\text{-22}$ and $(R_{\text{Ru}}S_{\text{P}}S_{\text{C}})\text{-22}$ as orange solids in 41% and 46% yields, respectively. Recrystallization of complex $(R_{\text{Ru}}R_{\text{P}}S_{\text{C}})\text{-22}$ and $(R_{\text{Ru}}S_{\text{P}}S_{\text{C}})\text{-22}$ from dichloromethane and diethyl ether gave red prisms. In CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $(R_{\text{Ru}}R_{\text{P}}S_{\text{C}})\text{-22}$ and $(R_{\text{Ru}}S_{\text{P}}S_{\text{C}})\text{-22}$ showed a singlet at δ 11.5 and 22.8, respectively.

3.2.3.1 X-ray Structural Analysis of Complex (*R*_{Ru}*R*_P*S*_C)-22

The single crystal X-ray structure of complex (*R*_{Ru}*R*_P*S*_C)-22 is shown in Figure 3-3. The geometry at ruthenium exhibits the "three-legged piano-stool" disposition; the η^6 -coordinated arene is in a "stool" position, while the "legs" comprise P and Cl atoms. The angles at the Ru center are in the range of 81.9(1)-87.1(1)°. Additionally, the geometry at palladium is a slightly distorted square planar with bond angles in the ranges of 83.7(1)-94.9(1)° and 172.8(1)-175.0(1)°, respectively. It is observed that the chloride bridge has been formed in the molecule. The bond lengths of Ru(1)-Cl(2) and Pd(1)-Cl(2) are 2.396(1) Å and 2.341(1) Å, respectively, and the angle of Ru(1)-Cl(2)-Pd(1) is 115.3(1)°. The unsaturated alkyne moiety of the alkynylphosphine has been inserted into the Pd-C bond of the cyclopalladated complex **15**, forming a new carbon-carbon bond between C(17) and C(19) and a new metal-carbon bond between Pd(1) and C(16). The absolute configuration at C(25) remained unchanged. Furthermore, two stereogenic centers at Ru(1) and P(1) both adopt the *R* absolute configurations. Selected bond distances and angles for complex (*R*_{Ru}*R*_P*S*_C)-22 are given in Table 3-3.

Figure 3-3 Molecular structure of complex ($R_{Ru}R_pS_C$)-22

Table 3-3 Selected Bond Lengths (Å) and Angles (deg) of ($R_{Ru}R_pS_C$)-22

Ru(1)-P(1)	2.335(1)	Ru(1)-Cl(1)	2.394(1)
Ru(1)-Cl(2)	2.396(1)	Pd(1)-Cl(2)	2.341(1)
Pd(1)-Cl(3)	2.433(1)	Pd(1)-N(1)	2.118(2)
Pd(1)-C(16)	2.019(2)	P(1)-C(7)	1.769(2)
P(1)-C(10)	1.828(2)	P(1)-C(16)	1.818(2)
C(7)-C(8)	1.194(3)	C(16)-C(17)	1.346(3)
P(1)-Ru(1)-Cl(1)	85.0 (1)	P(1)-Ru(1)-Cl(2)	81.9(1)
Cl(1)-Ru(1)-Cl(2)	87.1(1)	Cl(2)-Pd(1)-Cl(3)	83.7(1)
Cl(2)-Pd(1)-N(1)	175.0(1)	Cl(2)-Pd(1)-C(16)	89.7(1)
Cl(3)-Pd(1)-N(1)	91.6(1)	Cl(3)-Pd(1)-C(16)	172.8(1)
N(1)-Pd(1)-C(16)	94.9(1)	Ru(1)-P(1)-C(7)	108.9(1)

Ru(1)-P(1)-C(10)	117.1(1)	Ru(1)-P(1)-C(16)	112.3(1)
C(7)-P(1)-C(10)	101.8(1)	C(7)-P(1)-C(16)	113.4(1)
C(10)-P(1)-C(16)	102.9(1)	Ru(1)-Cl(2)-Pd(1)	115.3(1)

3.2.3.2 X-ray Structural Analysis of Complex ($R_{Ru}S_P S_C$)-**22**

The single crystal X-ray structure of complex ($R_{Ru}S_P S_C$)-**22** is shown in Figure 3-4. Like complex ($R_{Ru}R_P S_C$)-**22**, the geometry at ruthenium also exhibits the "three-legged piano-stool" disposition; the η^6 -coordinated arene is in a "stool" position, while the "legs" comprise P and Cl atoms. The angles at the Ru center are in the range of 82.4(1)-87.4(1)°. Additionally, the geometry at palladium is a slightly distorted square planar with bond angles in the ranges of 85.4(1)-93.7(2)° and 172.6(2)-175.1(2)°, respectively. It is observed that the chloride bridge was formed in the product. The bond lengths of Ru(1)-Cl(2) and Pd(1)-Cl(2) are 2.409(2) Å and 2.344(2) Å, respectively, and the angle of Ru(1)-Cl(2)-Pd(1) is 114.8(1)°. The unsaturated alkyne moiety of the alkynylphosphine has been inserted into the Pd-C bond of complex **15**, forming a new carbon-carbon bond between C(17) and C(19) and a new metal-carbon bond between Pd(1) and C(16). The absolute configuration at C(25) remained unchanged. Furthermore, one stereogenic center at Ru(1) adopts the *R* absolute configuration that is same as that of complex ($R_{Ru}R_P S_C$)-**22**. The stereogenic center at P(1) adopts the *S* absolute configuration which is different from that of complex ($R_{Ru}R_P S_C$)-**22**. Selected bond distances and angles for complex ($R_{Ru}S_P S_C$)-**22** are given in Table 3-4.

Figure 3-4 Molecular structure of complex ($R_{Ru}S_P S_C$)-22

Table 3-4 Selected Bond Lengths (Å) and Angles (deg) of ($R_{Ru}S_P S_C$)-22

Ru(1)-P(1)	2.320(2)	Ru(1)-Cl(1)	2.401(3)
Ru(1)-Cl(2)	2.409(2)	Pd(1)-Cl(2)	2.344(2)
Pd(1)-Cl(3)	2.404(2)	Pd(1)-N(1)	2.135(5)
Pd(1)-C(16)	2.001(5)	P(1)-C(7)	1.764(8)
P(1)-C(10)	1.817(7)	P(1)-C(16)	1.799(5)
C(7)-C(8)	1.185(12)	C(16)-C(17)	1.344(7)
P(1)-Ru(1)-Cl(1)	86.5(1)	P(1)-Ru(1)-Cl(2)	82.4(1)
Cl(1)-Ru(1)-Cl(2)	87.4(1)	Cl(2)-Pd(1)-Cl(3)	85.4(1)
Cl(2)-Pd(1)-N(1)	175.1(2)	Cl(2)-Pd(1)-C(16)	87.5(2)
Cl(3)-Pd(1)-N(1)	93.5(2)	Cl(3)-Pd(1)-C(16)	172.6(2)
N(1)-Pd(1)-C(16)	93.7(2)	Ru(1)-P(1)-C(7)	108.9(3)
Ru(1)-P(1)-C(10)	117.7(3)	Ru(1)-P(1)-C(16)	113.6(2)

C(7)-P(1)-C(10)	101.4(4)	C(7)-P(1)-C(16)	102.6(3)
C(10)-P(1)-C(16)	110.7(3)	Ru(1)-Cl(2)-Pd(1)	114.8(1)

3.2.3.3 Absolute Configurations at Ruthenium and Phosphorus in Complexes ($R_{Ru}R_P S_C$)-**22** and ($R_{Ru}S_P S_C$)-**22**

Complexes ($R_{Ru}R_P S_C$)-**22** and ($R_{Ru}S_P S_C$)-**22** resulting from the insertion process both contain two stereogenic centers at ruthenium and phosphorus. The formation of the chirality of ruthenium has been attributed to the formation of the chloride bridge, which makes the two chlorine atoms non-equivalent. The absolute configuration at ruthenium is same in each complex. Moreover, this ruthenium configuration is also same as that of complex **16**. Theoretically, the presence of two active chiral centers should give rise to two diastereomerically related pairs of enantiomers (Scheme 3-12). However the two possible diastereoisomers, ($S_{Ru}R_P S_C$)-**22** and ($S_{Ru}S_P S_C$)-**22**, bearing the *S* ruthenium center, were not observed during the insertion process. The fact that only the diastereomeric products, ($R_{Ru}R_P S_C$)-**22** and ($R_{Ru}S_P S_C$)-**22**, were isolated indicates that good steric control was present at ruthenium in the involved reaction. The reason for the stereoselectivity at ruthenium is the same as that in the case of complex **16**, which is believed to be affected by the chiral carbon neighboring the NMe₂ group.

Scheme 3-12

Since the insertion reaction converted only one of the two alkyne moieties into a C=C bond, a chiral center at phosphorus was formed after this process. The absolute configuration at phosphorus in complex $(R_{Ru}R_P S_C)\text{-22}$ is *R*, while that in complex $(R_{Ru}S_P S_C)\text{-22}$ is *S*. Moreover, in CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of crude reaction mixture showed two sharp singlets at δ 11.5 and 22.8 with a ratio of 1:1.1, which indicated that the two diastereoisomers were generated in similar yields.

3.2.4 Insertion Reaction of Dikynylphosphine Complex **3** and Nonchiral Palladium Dimer **9**, Synthesis of Complex **23**

Insertion reaction of the P-coordinated dialkynylphosphine complex **3** and nonchiral cyclopalladated dimer **9** has also been studied. Activated by the coordination of the

dialkynylphosphine to the ruthenium center, complex **3** underwent the insertion reaction with 0.5 equiv of organopalladium dimer **9** to give the product **23** (Scheme 3-13). When monitored by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, this reaction was found to be complete in 1 day at room temperature in dichloromethane. After the insertion, in CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture exhibited 2 singlets at δ 11.3 and 22.7 with a ratio of 1:1.7, which indicated that two diastereomerically related pairs of enantiomers formed (the product **23** includes two diastereomerically related pairs of enantiomers, see Section 3.2.4.1). The homometallic palladium complex similar to complex **20** has not been observed.

Scheme 3-13

The crude mixture was purified by silica gel column chromatography and the eluted fractions were then precipitated by diethyl ether to give $(R_{\text{Ru}}R_{\text{P}})\text{-}\mathbf{23}/(S_{\text{Ru}}S_{\text{P}})\text{-}\mathbf{23}$ and $(R_{\text{Ru}}S_{\text{P}})\text{-}\mathbf{23}/(S_{\text{Ru}}R_{\text{P}})\text{-}\mathbf{23}$ both as orange solids in 23% and 54% yields, respectively. In CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $(R_{\text{Ru}}R_{\text{P}})\text{-}\mathbf{23}/(S_{\text{Ru}}S_{\text{P}})\text{-}\mathbf{23}$ and $(R_{\text{Ru}}S_{\text{P}})\text{-}\mathbf{23}/(S_{\text{Ru}}R_{\text{P}})\text{-}\mathbf{23}$ showed a singlet at δ 11.3 and 22.7, respectively. Interestingly recrystallization of both complexes $(R_{\text{Ru}}R_{\text{P}})\text{-}\mathbf{23}/(S_{\text{Ru}}S_{\text{P}})\text{-}\mathbf{23}$ and $(R_{\text{Ru}}S_{\text{P}})\text{-}\mathbf{23}/(S_{\text{Ru}}R_{\text{P}})\text{-}\mathbf{23}$ from dichloromethane and

diethyl ether gave pure ($R_{Ru}S_P$)-**23**/ $(S_{Ru}R_P)$ -**23** as red prisms (This can indicate that there is equilibrium between these two diastereomerically related pairs of isomers, see Section 3.2.4.1).

3.2.4.1 Absolute Configuration of Complex **23** and the chemical equilibrium between the isomers

Complex **23** contains two stereogenic centers at ruthenium and phosphorus, which gives rise to two diastereomerically related pairs of enantiomers. The formation of the chirality at ruthenium has been attributed to the formation of the chloride bridge, which makes the two chlorine atoms non-equivalent. On the other hand, since the insertion reaction converts only one of the two alkyne moieties into a C=C bond, it is observed that the chiral center at phosphorus was formed after this process. The absolute configurations of the four isomers are designated as $R_P R_{Ru}$, $S_P S_{Ru}$, $R_P S_{Ru}$, $S_P R_{Ru}$, as shown in Scheme 3-14.

$(R_{Ru}R_P)$ -**23**/ $(S_{Ru}S_P)$ -**23** and $(R_{Ru}S_P)$ -**23**/ $(S_{Ru}R_P)$ -**23** are both stable in the solid state. However, in dichloromethane or chloroform solution, these two pairs of diastereoisomers could interconvert rapidly at room temperature (Scheme 3-14). When monitored by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, the chemical equilibrium was found to be attained within 10 h with the ratio of $(R_{Ru}R_P)$ -**23**/ $(S_{Ru}S_P)$ -**23** and $(R_{Ru}S_P)$ -**23**/ $(S_{Ru}R_P)$ -**23** being about 1:1.7 in the equilibrium state. Mechanistically, this conversion process includes the cleavage of the weak coordinative Pd-Cl bond of the chloride bridge, the subsequent formation of a

new chloride bridge between the Pd atom and the other free Cl atom, and the reversion of the flexible 7-membered ring in the molecule. Compared with complex **16** and **22** (see Section 3.2.1.2 and 3.2.3.3), the corresponding carbon neighboring the NMe₂ group in complex **23** is nonchiral. Therefore there are no stereochemical factors limiting the reversion of the 7-membered ring, which is responsible for the generation of the equilibrium between those isomers.

Scheme 3-14

3.2.4.2 X-ray Structural Analysis of Complexes (*R*_{Ru}*S*_P)-**23**/*(S*_{Ru}*R*_P)-**23**

The X-ray structure of complex (*S*_{Ru}*R*_P)-**23** is shown in Figure 3-5. Its enantiomer, (*R*_{Ru}*S*_P)-**23**, coexists in a ratio of 1:1 in each unit cell. The geometry at ruthenium exhibits the "three-legged piano-stool" disposition; the η⁶-coordinated arene is in a "stool"

position while the "legs" comprise P and Cl atoms. The angles at the Ru center are in the range of 81.4(1)-87.9(1)°. Additionally, the geometry at palladium is a slightly distorted square planar with bond angles in the ranges of 85.6(1)-94.0(2)° and 173.4(2)-177.8(2)°, respectively. It is observed that the chloride bridge has been formed in the molecule. The bond lengths of Ru(1)-Cl(2) and Pd(1)-Cl(2) are 2.404(2) Å and 2.340(2) Å, respectively, and the angle of Ru(1)-Cl(2)-Pd(1) is 115.8(1)°. The unsaturated alkyne moiety of the alkynylphosphine has been inserted into the Pd-C bond of the cyclopalladated complex **9**, forming a new carbon-carbon bond between C(17) and C(19) and a new metal-carbon bond between Pd(1) and C(16). The absolute configuration at C(25) remained unchanged. Furthermore, one stereogenic center at Ru(1) adopts the *S* absolute configuration in (*S*_{Ru}*R*_P)-**23**, as shown in Figure 3-5, while *R* in complex (*R*_{Ru}*S*_P)-**23**. Selected bond distances and angles for complexes (*R*_{Ru}*S*_P)-**23**/*S*_{Ru}*R*_P)-**23** are given in Table 3-5.

Figure 3-5 Molecular structure of complex (*S*_{Ru}*R*_P)-**23**

Table 3-5 Selected Bond Lengths (Å) and Angles (deg) of (*R*_{Ru}*S*_P)-23**/*(S*_{Ru}*R*_P)-**23****

Ru(1)-P(1)	2.335(1)	Ru(1)-Cl(1)	2.408(1)
Ru(1)-Cl(2)	2.404(1)	Pd(1)-Cl(2)	2.340(1)
Pd(1)-Cl(3)	2.408(1)	Pd(1)-N(1)	2.107(2)
Pd(1)-C(16)	2.015(2)	P(1)-C(7)	1.772(2)
P(1)-C(10)	1.827(2)	P(1)-C(16)	1.816(2)
C(7)-C(8)	1.187(3)	C(16)-C(17)	1.346(2)
P(1)-Ru(1)-Cl(1)	87.7 (1)	P(1)-Ru(1)-Cl(2)	81.4(1)
Cl(1)-Ru(1)-Cl(2)	87.9(1)	Cl(2)-Pd(1)-Cl(3)	85.6(1)
Cl(2)-Pd(1)-N(1)	177.8(1)	Cl(2)-Pd(1)-C(16)	88.2(1)
Cl(3)-Pd(1)-N(1)	92.3(1)	Cl(3)-Pd(1)-C(16)	173.4(1)
N(1)-Pd(1)-C(16)	94.0(1)	Ru(1)-P(1)-C(7)	109.0(1)
Ru(1)-P(1)-C(10)	113.6(1)	Ru(1)-P(1)-C(16)	113.0(1)
C(7)-P(1)-C(10)	100.7(1)	C(7)-P(1)-C(16)	102.8(1)
C(10)-P(1)-C(16)	116.2(1)	Ru(1)-Cl(2)-Pd(1)	115.8(1)

3.2.5 Double Insertion Studies on Complex **22**

The reaction of the diastereomeric complex (*R*_{Ru}*R*_P*S*_C)-**22** and nonchiral cyclopalladated dimer **9** has been studied. This reaction leads to the insertion of both triple bonds in the P-coordinated dialkynylphosphine complex **3** into the Pd-C bonds of

complexes **9** and **15** to generate a double insertion product. Under mild condition, the remaining unreacted alkynyl group of ($R_{Ru}R_{P}S_C$)-**22** was observed to insert into the Pd-C bond of organopalladium complex **9** to give the trimetallic complex **24**. When monitored using the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, this reaction was found to be complete in 2 days at 40 °C in chloroform. After insertion, in CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture exhibited a singlet at δ 41.0 (Scheme 3-15).

Scheme 3-15

The crude mixture was purified by silica gel column chromatography and then precipitated by diethyl ether to give **24** as an orange solid in 51% yield. In CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **24** showed a singlet at δ 41.0. The single crystal of **24** could not be obtained, although the structure could be established by many other analyses. The structure shown in Scheme 3-15 is in accordance with a series of ^1H , ^{31}P , $^1\text{H}\{^{31}\text{P}\}$, and 2D ROESY NMR studies and elemental analysis.

Scheme 3-16 shows the numbering scheme of complex **24** used in the 2D ROESY NMR analysis, some chlorine atoms are omitted for clarity. Selected ^{31}P and ^1H NMR

data of complex **24** are given in Table 3-6. These NMR assignments are based on a series of ^1H , ^{31}P , $^1\text{H}\{^{31}\text{P}\}$, and 2D ROESY NMR studies. Figure 3-6 shows the 2D ^1H - ^1H ROESY NMR spectrum of complex **24**.

Scheme 3-16

In the 2D ROESY NMR spectrum of complex **24**, the interactions (C, D) between Me25 and the two NMe(Me26) groups are clear. For the two NMe groups, only the equatorial NMe [Me26(eq)], rather than the axial NMe [Me26(ax)], interacts with H25 to generate the signal H. These NOE signals reflect that Me25 and H25 occupy the equatorial and axial position, respectively. Moreover, other expected interactions involving Me25, Me26(ax), and the neighboring phenyl proton H23 [U, Me25-H23; P, Me26(ax)-H23], are also observed in the 2D ROESY NMR spectrum. Similarly, the NOE signals due to the interactions involving H8, Me7, and H10 have also been recorded. The interactions of F [H8(eq)-Me7(eq)], G [H8(eq)-Me7(ax)], and L [H8(ax)-Me7(eq)] are

clear, while the interaction of H8(ax)-Me7(ax) could not be observed. Furthermore, the equatorial H8 and axial Me7 interact with the aromatic proton, H10, generating the signals O [H8(eq)-H10] and Q [Me7(ax)-H10], respectively.

Figure 3-6. Two-dimensional ^1H ROESY NMR spectrum of complex **24** in CDCl_3 . All off-diagonal peaks are of negative intensity. Selected NOE contacts: A, Me18-Me15; B, Me15-Me26(eq); C, Me25-Me26(ax); D, Me25-Me26(eq); E, Me7(ax)-Me7(eq); F, H8(eq)-Me7(eq); G, H8(eq)-Me7(ax); H, H25-Me26(eq); I, H25-Me15; J, H25-Me25; K, H8(eq)-H8(ax); L, H8(ax)-Me7(eq); M, C_6H_6 -Me7(eq); N, H16-H8(ax); O, H8(eq)-H10; P, Me26(ax)-H23; Q, Me7(ax)-H10; R, H16-Me18; S, Me26(eq)-H3; T, Me18-H20; U,

Me25-H23; V, Me15-H13; W, H13-H12; X, H5-H4; Y, H2-H3; Z, H2- C₆H₆; Δ, H2-Me26(eq).

Table 3-6. Selected ³¹P and ¹H NMR Spectrum Chemical Shift Values of complex 24 in CDCl₃ (coupling constants in Hz are given in parentheses)

24	
³¹ P	41.0 s.
NCHMe	1.29 d, (³ J _{HH} = 7.0)
NCHMe	4.02 q (³ J _{HH} = 7.0)
CHH(eq)	3.21 d, (² J _{HH} = 14.1)
CHH(ax)	4.74 d, (² J _{HH} = 14.1)
Pd-C=C-Me	1.95 d, (⁴ J _{PH} = 2.7)
H-C=C-Me	2.21 s.
C(MeH)NMe(ax)	2.59 s.
C(MeH)NMe(eq)	2.63 s.
CH ₂ NMe(ax)	2.37 s.
CH ₂ NMe(eq)	2.97 s
C ₆ H ₆	5.70 s
H-C=C-Me	7.05 d, (² J _{PH} = 18.3)
H ₁₃	7.79-7.81, m
H ₅	7.84 d, (³ J _{HH} = 8.6)
H ₂	10.54 dd, (³ J _{HH} = 7.9, ³ J _{PH} = 7.9)

The interactions involving the substituents on the two alkene moieties have also been recorded. The two methyl groups, Me15 and Me18, interact with their corresponding neighboring phenyl proton to generate the signals V (Me15-H13) and T (Me18-H20), respectively. Moreover, a strong interaction (N) has also been found due to the extreme proximity between H16 and H8(ax). It is noteworthy that there are signals A (Me18-Me15) and R (H16-Me18) in the 2D ROESY NMR spectrum, indicating the short distance between the two involved alkene moieties.

The coordinated benzene interacts with Me7(eq), thus leading to the formation of the signal M. However, the interaction between the coordinated benzene and Me15 could not be observed in this spectrum. The involved NOE interaction indicates that the ruthenium center is closer to Me7 than Me15, which thus deduces that the absolute configuration at ruthenium was retained after the insertion process.

The other NOE signals are also clear and summarized in the caption of Figure 3-6. In conclusion, the 2D ROESY NMR spectrum is agreement with the interactions expected from the structure shown in Scheme 3-16.

The free alkyne moiety of another diastereomeric complex ($R_{Ru}S_P S_C$)-**22** was found to be inert to the second insertion into the Pd-C bond of complex **9** under similar conditions. The possible reason is the hindrance resulting from the equatorial NMe group. Furthermore, both ($R_{Ru}R_P S_C$)-**22** and ($R_{Ru}S_P S_C$)-**22** failed to react with the chiral palladacycle **15** under similar conditions to give the double insertion products. This is a

clear indication that the steric factors play a major role in the second insertion process.

3.3 Conclusions

Coordination of an alkynylphosphine to a ruthenium center successfully activated the insertion of its alkyne moiety into the Pd-C bond of cyclopalladated complexes containing chiral or nonchiral amine auxiliary. All of the reactions were carried out under mild conditions, which indicated their high reactivities. It is noteworthy that the chiral organopalladium dimer resulted in the formation of products containing a stable stereogenic center at ruthenium. Moreover, in the cases involving the P-coordinated dialkynylphosphine complex, products bearing two stereogenic centers at phosphorus and ruthenium were generated after insertion process. Unfortunately, the stereoselectivity for the phosphorus center is not high.

Intrigued by the results obtained, a double insertion by utilizing the remaining unreacted alkyne moiety of the insertion products resulting from the dialkynylphenylphosphine complex has also been studied. Only the reaction of ($R_{Ru}R_{P}S_C$)-**22** and nonchiral cyclopalladated dimer **9** occurred and gave the trimetallic double insertion product **24**.

3.4 Experimental

The dimeric benzylamine palladium(II) complex **15** was prepared according to the standard literature method.³¹²

Synthesis of Complex 16

Method 1, from complex 5 and 15

Complex **5** $\text{Ru}(\eta^6\text{-benzene})\{\text{PPh}_2(\text{C}\equiv\text{CCH}_3)\}\text{Cl}_2$ (0.112 g, 0.24 mmol) was stirred with cyclopalladated complex **15** (0.069 g, 0.12 mmol) in dichloromethane (10 mL) for 2 days. The resulting solution was then concentrated and purified by silica gel column chromatography (diethyl ether-dichloromethane 1:3, and then acetone-dichloromethane, 1:3). The subsequent precipitation by diethyl ether gave **16** as an orange solid. Yield: 0.091 g (51%). Complex **16** was recrystallized from dichloromethane and diethyl ether as red prisms, which were suitable for X-ray analysis. Additionally, by-product **17** was also isolated during silica gel column chromatography (diethyl ether-dichloromethane 1:3) as a yellow solid. Yield: 0.018 g (10%). For **16**: Mp: 205-207 °C dec. $[\alpha]_{\text{D}} +332.0^\circ$ (*c* 0.5, CHCl_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 60.0 (s). ^1H NMR (CDCl_3 , δ): 1.27 (d, $^3J_{\text{HH}} = 7.0$ Hz, 3H, NCHMe); 1.48 (3H), 2.18 (3H) (s, NMe); 2.52 (s, 3H, $\text{C}=\text{C-Me}$); 4.08 (q, $^3J_{\text{HH}} = 7.0$ Hz, 1H, NCHMe); 5.47 (s, 6H, C_6H_6); 7.18-7.28 (m, 2H), 7.32-7.36 (m, 2H), 7.49-7.60 (m, 6H), 7.93 (br.s, 2H), 9.13 (br.s, 2H), (*aromatics*). Anal. Calcd for $\text{C}_{31}\text{H}_{33}\text{Cl}_3\text{NPPdRu}$: C, 48.7; H, 4.4; N, 1.8. Found: C, 48.6; H, 4.6; N, 1.9. For **17**: $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 13.0 (s). ^1H NMR (CDCl_3 , δ): 1.04 (d, $^3J_{\text{HH}} = 7.1$ Hz, 3H, NCHMe); 1.75 (d, $^4J_{\text{PH}} = 2.1$ Hz, 3H, $\text{C}=\text{C-Me}$); 1.87 (s, 3H, NMe); 2.16 (d, $^3J_{\text{HH}} = 7.0$ Hz, 3H, NCHMe); 2.56 (m, 6H,

NMe); 3.00 (d, $^4J_{\text{PH}} = 3.7$ Hz, 3H, NMe); 3.50 (1H), 3.70 (1H) (q, $^3J_{\text{HH}} = 7.0$ Hz, 1H, NCHMe); 6.43 (dd, $^3J_{\text{HH}} = 7.1$ Hz, $^4J_{\text{PH}} = 7.1$ Hz, 1H), 6.52 (t, $^3J_{\text{HH}} = 7.3$ Hz, 1H), 6.89 (td, $^3J_{\text{HH}} = 7.3$ Hz, $^4J_{\text{HH}} = 0.8$ Hz, 1H), 7.05 (dd, $^3J_{\text{HH}} = 7.4$ Hz, $^4J_{\text{HH}} = 1.4$ Hz, 1H), 7.21 (m, 2H); 7.32-7.53 (m, 8H), 7.96 (m, 2H), 8.09 (dd, $^3J_{\text{PH}} = 11.1$ Hz, $^3J_{\text{PH}} = 7.9$ Hz, 2H) (*aromatics*).

Method 2, from complex **2** and **18**

The complex $[(\eta^6\text{-benzene})\text{RuCl}_2]_2$ **2** (0.019 g, 0.038 mmol) was stirred with complex **18** (0.040 g, 0.077 mmol) in dichloromethane (4 mL) for 2 days. The resulting solution was then concentrated and purified by silica gel column chromatography (diethyl ether-dichloromethane 1:3, and then acetone-dichloromethane, 1:3). The subsequent precipitation by diethyl ether gave **16** as an orange solid. Yield: 0.007 g (11%). Additionally, by-products **5** and **17** were also isolated during silica gel column chromatography (diethyl ether-dichloromethane 1:3) as a yellow solid. Yield: **5**, 0.006 g (15%); **17**, 0.020 g (32%).

Synthesis of Complex **19**

Method 1, from complex **5** and **9**

Complex **5** $\text{Ru}(\eta^6\text{-benzene})\{\text{PPh}_2(\text{C}\equiv\text{CCH}_3)\}\text{Cl}_2$ (0.121 g, 0.25 mmol) was stirred with cyclopalladated complex **9** (0.071 g, 0.13 mmol) in dichloromethane (12 mL) for 2 days. The resulting solution was then concentrated and purified by silica gel column chromatography (diethyl ether-dichloromethane 1:3, and then acetone-dichloromethane, 1:3). The subsequent precipitation by diethyl ether gave **19** as an orange solid. Yield:

0.123 g (65%). Additionally, by-product **20** was also isolated during silica gel column chromatography (diethyl ether-dichloromethane 1:3) as a yellow solid. Yield: 0.008 g (4%). Complex **20** was recrystallized from dichloromethane and diethyl ether as yellow prisms, which were suitable for X-ray analysis. For **19**: Mp: 205-207 °C dec. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 60.0 (s). ^1H NMR (CDCl_3 , δ): 1.46 (3H), 2.08 (3H) (s, *NMe*); 2.57 (s, 3H, *C=C-Me*); 2.82 (d, $^2J_{\text{HH}} = 10.3$ Hz, 1H), 3.71 (d, $^2J_{\text{HH}} = 10.3$ Hz, 1H) (*NCHH*); 5.50 (s, 6H, *C₆H₆*); 7.07-7.09 (m, 1H), 7.14-7.17 (m, 1H), 7.32-7.36 (m, 2H), 7.48-7.58 (m, 6H), 7.91 (br.s, 2H), 9.12 (br.s, 2H), (*aromatics*). Anal. Calcd for $\text{C}_{30}\text{H}_{31}\text{Cl}_3\text{NPPdRu}$: C, 48.0; H, 4.2; N, 1.9. Found: C, 48.1; H, 4.5; N, 1.9. For **20**: Mp: 188-190 °C dec. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 15.0 (s). ^1H NMR (CDCl_3 , δ): 1.72 (d, $^4J_{\text{PH}} = 2.1$ Hz, 3H, *C=C-Me*); 1.80 (s, 3H, *NMe*); 2.43 (d, $^2J_{\text{HH}} = 10.9$ Hz, 1H, *NCHH*); 2.58-2.61 (m, 6H), 3.11 (d, $^4J_{\text{PH}} = 3.5$ Hz, 3H) (*NMe*); 3.28 (d, $^2J_{\text{HH}} = 10.9$ Hz, 1H), 3.50 (d, $^2J_{\text{HH}} = 13.7$ Hz, 1H), 4.69 (d, $^2J_{\text{HH}} = 13.7$ Hz, 1H) (*NCHH*); 6.45 (dd, $^3J_{\text{HH}} = 7.2$ Hz, $^4J_{\text{PH}} = 7.2$ Hz, 1H), 6.51 (t, $^3J_{\text{HH}} = 7.5$ Hz, 1H), 6.87 (t, $^3J_{\text{HH}} = 7.1$ Hz, 1H), 7.01 (d, $^3J_{\text{HH}} = 7.3$ Hz, 1H), 7.06 (d, $^3J_{\text{HH}} = 7.5$ Hz, 1H), 7.19-7.22 (m, 1H); 7.38-7.53 (m, 8H), 7.92-7.96 (m, 2H), 8.15 (dd, $^3J_{\text{PH}} = 11.4$ Hz, $^3J_{\text{PH}} = 7.4$ Hz, 2H) (*aromatics*). Anal. Calcd for $\text{C}_{33}\text{H}_{37}\text{Cl}_2\text{N}_2\text{PPd}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$: C, 49.1; H, 4.7; N, 3.4. Found: C, 48.7; H, 5.1; N, 3.4.

Method 2, from complex **2** and **21**

The complex $[(\eta^6\text{-benzene})\text{RuCl}_2]_2$ **2** (0.049 g, 0.099 mmol) was stirred with complex **21** (0.098 g, 0.196 mmol) in dichloromethane (10 mL) for 2 days. The resulting solution was then concentrated and purified by silica gel column chromatography (diethyl ether-dichloromethane 1:3, and then acetone-dichloromethane, 1:3), and the

subsequent precipitation of the eluted fraction by diethyl ether gave **19** as an orange solid. Yield: 0.051 g (35%). Additionally, by-product **5** and **20** were also isolated during silica gel column chromatography (diethyl ether-dichloromethane 1:3) as a yellow solid. Yield: **5**, 0.013 g (14%); **20**, 0.029 g (19%).

Synthesis of Complex **20** from complex **21** and **9**

Cyclopalladated complex **9** (0.058 g, 0.11 mmol) was stirred with complex **21** (0.105 g, 0.21 mmol) in dichloromethane (10 mL) for 6 days. Removal of solvent and the subsequent precipitation by diethyl ether gave pure **20** as a yellow solid. Yield: 0.170 g (100%). Complex **20** was recrystallized from dichloromethane and diethyl ether as yellow prisms, which were suitable for X-ray analysis.

Synthesis of Complex (*R*_{Ru}*R*_P*S*_C)-**22** and (*R*_{Ru}*S*_P*S*_C)-**22**

Complex **3** Ru(η^6 -benzene){PPh(C $\equiv$ CCH₃)₂}Cl₂ (0.100 g, 0.23 mmol) was stirred with cyclopalladated complex **15** (0.067 g, 0.12 mmol) in dichloromethane (20 mL) for 1 day. The resulting solution was then concentrated and purified by silica gel column chromatography (acetone-dichloromethane, 1:3), and the subsequent precipitation by diethyl ether gave (*R*_{Ru}*R*_P*S*_C)-**22** and (*R*_{Ru}*S*_P*S*_C)-**22** both as orange solids. Yield: (*R*_{Ru}*R*_P*S*_C)-**22**, 0.068 g (41%); (*R*_{Ru}*S*_P*S*_C)-**22**, 0.077 g (46%). Complex (*R*_{Ru}*R*_P*S*_C)-**22** and (*R*_{Ru}*S*_P*S*_C)-**22** were recrystallized from dichloromethane and diethyl ether as red prisms, which were suitable for X-ray analysis, respectively. For (*R*_{Ru}*R*_P*S*_C)-**22**: Mp: 225-226 °C dec. [α]_D +492.9° (*c* 1.0, CHCl₃). ³¹P{¹H} NMR (CDCl₃, δ): 11.5 (s). ¹H NMR (CDCl₃, δ): 1.10 (d, ³J_{HH} = 7.0 Hz, 3H, NCHMe); 1.64 (s, 3H NMe); 2.20 (d, ⁴J_{PH} = 3.5 Hz, 3H,

PCC-Me); 2.34 (s, 3H NMe); 2.58 (d, $^4J_{\text{PH}} = 2.8$ Hz, 3H, C=C-Me); 3.89 (q, $^3J_{\text{HH}} = 7.0$ Hz, 1H, NCHMe); 5.55 (s, 6H, C_6H_6); 7.13-7.15 (2H), 7.25-7.30 (1H), 7.38-7.40 (1H), 7.49-7.54 (1H), 7.61-7.66 (2H), 8.79-8.85 (2H), (m, *aromatics*). Anal. Calcd for $\text{C}_{28}\text{H}_{31}\text{Cl}_3\text{NPPdRu}$: C, 46.3; H, 4.3; N, 1.9. Found: C, 46.6; H, 4.4; N, 1.9. For ($R_{\text{Ru}}S_{\text{P}}S_{\text{C}}$)-**22**: Mp: 227-228 °C dec. $[\alpha]_{\text{D}} +447.5^\circ$ (c 0.6, CHCl_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 22.8 (s). ^1H NMR (CDCl_3 , δ): 1.39 (d, $^3J_{\text{HH}} = 7.0$ Hz, 3H, NCHMe); 1.46 (d, $^4J_{\text{PH}} = 2.8$ Hz, 3H, C=C-Me); 2.26 (d, $^4J_{\text{PH}} = 3.5$ Hz, 3H, PCC-Me); 2.65 (3H), 3.16 (3H) (s, NMe); 4.28 (q, $^3J_{\text{HH}} = 7.0$ Hz, 1H, NCHMe); 5.70 (s, 6H, C_6H_6); 7.16-7.26 (4H), 7.45-7.44 (3H), 8.19-8.25 (2H), (m, *aromatics*). Anal. Calcd for $\text{C}_{28}\text{H}_{31}\text{Cl}_3\text{NPPdRu}\cdot 0.5\text{CH}_2\text{Cl}_2$: C, 44.5; H, 4.2; N, 1.8. Found: C, 44.8; H, 4.4; N, 2.2.

Synthesis of Complex 23

Complex **3** $\text{Ru}(\eta^6\text{-benzene})\{\text{PPh}(\text{C}\equiv\text{CCH}_3)_2\}\text{Cl}_2$ (0.20 g, 0.45 mmol) was stirred with cyclopalladated complex **9** (0.13 g, 0.23 mmol) in dichloromethane (40 mL) for 1 day. The resulting solution was then concentrated and purified by silica gel column chromatography (acetone-dichloromethane, 1:4), and the subsequent precipitation by diethyl ether gave ($R_{\text{Ru}}R_{\text{P}}$)-**23**/ $(S_{\text{Ru}}S_{\text{P}})$ -**23** and ($R_{\text{Ru}}S_{\text{P}}$)-**23**/ $(S_{\text{Ru}}R_{\text{P}}$)-**23** both as orange solids. Yield: ($R_{\text{Ru}}R_{\text{P}}$)-**23**/ $(S_{\text{Ru}}S_{\text{P}})$ -**23**, 0.081 g (23%); ($R_{\text{Ru}}S_{\text{P}}$)-**23**/ $(S_{\text{Ru}}R_{\text{P}}$)-**23**, 0.175 g (54%). Recrystallization of complex ($R_{\text{Ru}}R_{\text{P}}$)-**23**/ $(S_{\text{Ru}}S_{\text{P}})$ -**23** and ($R_{\text{Ru}}S_{\text{P}}$)-**23**/ $(S_{\text{Ru}}R_{\text{P}}$)-**23** from dichloromethane and diethyl ether both gave pure ($R_{\text{Ru}}S_{\text{P}}$)-**23**/ $(S_{\text{Ru}}R_{\text{P}}$)-**23** as red prisms, which were suitable for X-ray analysis, respectively.. For ($R_{\text{Ru}}R_{\text{P}}$)-**23**/ $(S_{\text{Ru}}S_{\text{P}})$ -**23**: Mp: 215-216 °C dec. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 11.3 (s). ^1H NMR (CDCl_3 , δ): 1.59 (s, 3H, NMe); 2.21 (d, $^4J_{\text{PH}} = 3.5$ Hz, 3H, PCC-Me); 2.43 (s, 3H, NMe); 2.59-2.61 (m, 4H,

NCHH and C=C-Me); 3.52 (d, $^2J_{\text{HH}} = 10.8$ Hz, 1H, NCHH); 5.58 (s, 6H, C_6H_6); 6.99-7.01 (1H), 7.12-7.17 (1H), 7.32-7.37 (1H), 7.44-7.56 (2H), 7.63-7.68 (2H), 8.81-8.88 (2H) (m, *aromatics*). Anal. Calcd for $\text{C}_{27}\text{H}_{29}\text{Cl}_3\text{NPPdRu}\cdot 0.5\text{CH}_2\text{Cl}_2$: C, 43.8; H, 4.0; N, 1.9. Found: C, 43.9; H, 4.3; N, 1.9. For ($R_{\text{Ru}}S_{\text{P}}$)-**23**/ $(S_{\text{Ru}}R_{\text{P}})$ -**23**: Mp: 220-221 °C dec. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 22.7 (s). ^1H NMR (CDCl_3 , δ): 1.45 (d, $^4J_{\text{PH}} = 2.6$ Hz, 3H, C=C-Me); 2.25 (d, $^4J_{\text{PH}} = 3.4$ Hz, 3H, PCC-Me); 2.69 (s, 3H, NMe); 3.01 (d, $^2J_{\text{HH}} = 10.8$ Hz, 1H, NCHH); 3.11 (s, 3H, NMe); 3.94 (d, $^2J_{\text{HH}} = 10.8$ Hz, 1H, NCHH); 5.71 (s, 6H, C_6H_6); 7.09-7.18 (2H), 7.26-7.28 (2H), 7.43-7.52 (3H), 8.14-8.21 (2H) (m, *aromatics*). Anal. Calcd for $\text{C}_{27}\text{H}_{29}\text{Cl}_3\text{NPPdRu}$: C, 45.5; H, 4.1; N, 2.0. Found: C, 45.1; H, 4.5; N, 1.9.

Double Insertion Reaction

Synthesis of Complex **24**

Complex ($R_{\text{Ru}}R_{\text{P}}S_{\text{C}}$)-**22** (0.570, 0.78 mmol) was stirred with nonchiral cyclopalladated complex **9** (0.219 g, 0.40 mmol) in chloroform (60 mL) at 40°C for 2 days. The resulting solution was then concentrated and purified by silica gel column chromatography (acetone-dichloromethane, 1:6), and the subsequent precipitation by diethyl ether gave pure **24** as an orange solid. Yield: 0.411 g (51%). Mp: 190-192 °C dec. $[\alpha]_{578} +38.4^\circ$ (c 0.9, CHCl_3). $[\alpha]_{546} +98.8^\circ$ (c 0.9, CHCl_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 41.0 (s). ^1H NMR (CDCl_3 , δ): 1.29 (d, $^3J_{\text{HH}} = 7.0$ Hz, 3H, NCHMe); 1.95 (d, $^4J_{\text{PH}} = 2.7$ Hz, 3H, PdC=CMe); 2.21 (s, 3H, HC=CMe); 2.37 (s, 3H), 2.59 (s, 3H), 2.63 (s, 3H), 2.97 (s, 3H) (NMe); 3.21 (d, $^2J_{\text{HH}} = 14.1$ Hz, 1H, NCHH); 4.02 (q, $^3J_{\text{HH}} = 7.0$ Hz, 1H, NCHMe); 4.74 (d, $^2J_{\text{HH}} = 14.1$ Hz, 1H, NCHH); 5.70 (s, 6H, C_6H_6); 7.05 (d, $^2J_{\text{PH}} = 18.3$

Hz, 1H, $PCH=CMe$); 7.17-7.85 (m, 9H), 7.79-7.81 (m, 1H), 7.84 (d, $^3J_{HH} = 8.6$ Hz, 1H), 10.54 (dd, $^3J_{HH} = 7.9$ Hz, $^3J_{PH} = 7.9$ Hz, 1H) (*aromatics*). Anal. Calcd for $C_{37}H_{43}Cl_4N_2PPd_2Ru \cdot 0.5CH_2Cl_2$: C, 43.1; H, 4.2; N, 2.7. Found: C, 43.1; H, 4.5; N, 2.9.

Chapter 4

Hydration Reactions of the Bimetallic Ruthenium(II)-Palladium(II) Complexes Bearing a Free Alkyne Moiety

4.1 Introduction

Hydration of alkynes is one of the simplest and most convenient ways to generate carbonyl compounds. An advantage of this process is the use of water as reactant. This process is normally slow in aqueous acid,¹⁷⁰ but can be accelerated by the addition of a mercuric salts.¹⁷¹⁻¹⁷³ Additionally, other catalysts such as ion-exchange resins containing Hg(II), Cu(I), Zn(II), or Cd(II),¹⁷⁴⁻¹⁷⁷ many metal phosphates, transition metal phosphomolybdates,¹⁷⁸ heteropoly acids (HPAs),^{179, 180} and zeolite catalysts containing a variety of transition metal ions^{170, 181} also have potential in this process. Moreover, transition metal complexes, as a very important class of homogenous catalyst, have already been widely studied and applied in hydration reactions. A variety of transition metal complexes, such as Ru(II),^{186, 187, 212} Ru(III),¹⁸³ Rh(III),¹⁸⁹⁻¹⁹¹ Pd(II),¹⁹³⁻¹⁹⁶ Pt(II)¹⁹⁷⁻²⁰¹, Pt(IV),²⁰²⁻²⁰⁴ Cu(II),¹⁹³ and Au(I and III)^{195, 205-209} are able to catalyze the addition of water across an alkyne to give the desired carbonyl compound in a Markovnikov or *anti*-Markovnikov manner. One method to control the regioselectivity is based on the electronic properties of the ligands in the metal catalysts. The presence of the π -acidic COD ligand in the indenyl ruthenium(II) complex, (η^5 -C₉H₇)Ru(COD)Cl,

avored a π -alkyne intermediate that directed the addition of water in a Markovnikov fashion.¹⁸⁷ In contrast, the electron rich bisphosphine complex, $(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\text{PPh}_3)_2\text{Cl}$, which favored a vinylidene intermediate, drove the addition of water to both terminal alkynes and propargyl alcohols in an *anti*-Markovnikov manner when the reaction is performed at 60 ° C in an aqueous micellar environment.²¹⁶ Apart from catalytic processes on organic compounds, there are examples of hydration of an alkyne moiety in organometallic complexes. For examples, ketonyl and acyl ruthenium complexes have been reported to be prepared through hydration of acetylide ruthenium complexes.³²⁴⁻³²⁷ The enol and keto iridium complexes could also be isolated as the tautomer intermediates during hydration of tetrolic acid ethyl ester by optimizing the conditions of the isolation.³²⁸

Chapter 3 introduces the preparation of the bimetallic ruthenium(II)-palladium(II) complexes through the insertion reactions. For the P-coordinated dialkynylphosphine complex **3**, one of the two alkyne moieties was functionalized through the insertion reactions with cyclopalladated complexes involving benzylamines. In the present chapter, the remaining unreacted alkynyl group was converted into a ketonyl group through the hydration reaction, thus yielding a bifunctionalized phosphine complex. It should be noted that the absolute configuration at phosphorus remained unchanged in these products. Furthermore, this process also generated an unusual Pd-C-P-C 4-membered ring adopting a slightly distorted planar geometry, which was identified by X-ray crystallographic analysis. Additionally, the resulting hydration products are zwitterionic bimetallic ruthenium(II)-palladium(II) complexes, which have a positive charge at

ruthenium and a negative charge at palladium.

4.2 Results and Discussion

4.2.1 Hydration Reaction of Nonchiral Insertion Product **23**, Synthesis of Complex **25**

Heterobimetallic ruthenium(II)-palladium(II) complex **23**, which resulted from the insertion reaction, underwent a hydration reaction to give the product **25** (Scheme 4-1). When monitored by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, this reaction was found to be complete in 5 days at room temperature in a mixed solvent system of dichloromethane, acetone, and water (2:10:1). After hydration, in CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture exhibited a singlet at δ 49.8.

Scheme 4-1

Removal of organic solvents under vacuum followed by extraction with dichloromethane gave the crude mixture. This crude mixture was then purified by silica gel column chromatography, and the subsequent precipitation by diethyl ether gave **25** as

a yellow solid in 34% yield. Recrystallization of complex **25** from dichloromethane and diethyl ether gave orange prisms. In CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **25** showed a singlet at δ 49.8.

4.2.1.1 Absolute Configuration of Complex **25**

There are three chiral centers at ruthenium, phosphorus, and carbon in the structure of complex **25**. However, only the racemates, $(R_{\text{Ru}}R_{\text{P}}S_{\text{C}})$ -**25** and $(S_{\text{Ru}}S_{\text{P}}R_{\text{C}})$ -**25**, were formed and were subsequently isolated after hydration. The structures of this pair of enantiomers are shown in Scheme 4-2.

Scheme 4-2

Two steric factors are suggested to lead to the formation of $(R_{\text{Ru}}R_{\text{P}}S_{\text{C}})$ -**25** and $(S_{\text{Ru}}S_{\text{P}}R_{\text{C}})$ -**25**, as illustrated in Scheme 4-3. Firstly, the reversion of the chirality at

ruthenium will result in proximity between the chlorine atom and the NMe group and thus will generate repulsion between them (Scheme 4-3a). Secondly, the reversion of the chirality at carbon is also sterically unfavored since the acetyl group will occupy the *cis* position to the phenyl group on phosphorus after this reversion, which would be a repulsion interaction (Scheme 4-3b, L = ligand). Furthermore, as illustrated in Scheme 4-3b, the chelation of the ketonylphosphine to ruthenium would be difficult due to the necessary structural distortions involved.

Scheme 4-3

4.2.1.2 X-ray Structural Analysis of Complex 25

The single crystal X-ray structure of complex **25** is shown in Figure 4-1. A pair of enantiomers exists with a ratio of 1:1 in each unit cell. The geometry at ruthenium center exhibits the expected and usual "three-legged piano-stool" disposition. The η^6 -coordinated arene is in a "stool" position, while the "legs" comprise P, Cl, and O atoms. The angles at the Ru center are in the range of 80.7(1)-88.8(1)°. Ru(1)-O(1) [2.109(2) Å]

has slightly shorter bond length than the other two bonds connecting Ru(1) with P(1) and Cl(2), which have bond lengths of 2.306(1) Å [Ru(1)-P(1)] and 2.397(1) Å [Ru(1)-Cl(2)], respectively. There is a 4-membered ring adopting a slightly distorted planar geometry, which is composed of Pd(1), P(1), C(9), and C(16), in this molecule. The four angles at the vertexes of this 4-membered ring, C(9)-Pd(1)-C(16) [76.7(1)°], P(1)-C(9)-Pd(1) [89.2(1)°], C(9)-P(1)-C(16) [91.8(1)°], and P(1)-C(16)-Pd(1) [94.2(1)°] are distinctly smaller than those observed in normal geometry, which is attributed to the ring constraints. Additionally, the bond length of C(8)-O(1) is 1.260(4) Å, which indicates the generation of a double bond between these two atoms.³²⁴ Therefore a carbonyl group, instead of an enol moiety, has been formed in the product. Moreover, it is noteworthy that the C(8)-C(9) bond length is only 1.435(5) Å, which is shorter than the normal carbon-carbon single bond length. The absolute configuration of the structure shown in Figure 4-1 is designated as $R_{Ru}R_P S_C$, while its enantiomer adopts the $S_{Ru}S_P R_C$ absolute configuration. Selected bond distances and angles for complex **25** are given in Table 4-1.

Figure 4-1 Molecular structure of complex **25**

Table 4-1 Selected Bond Lengths (Å) and Angles (deg) of 25

Pd(1)-C(9)	2.149(3)	Pd(1)-C(16)	2.010(3)
Pd(1)-N(1)	2.145(3)	Pd(1)-Cl(1)	2.426(1)
Ru(1)-O(1)	2.109(2)	Ru(1)-P(1)	2.306(1)
Ru(1)-Cl(2)	2.397(1)	P(1)-C(9)	1.805(3)
P(1)-C(10)	1.824(3)	P(1)-C(16)	1.790(3)
O(1)-C(8)	1.260(4)	C(8)-C(9)	1.435(5)
C(16)-C(17)	1.330(4)		
C(9)-Pd(1)-C(16)	76.7(1)	C(9)-Pd(1)-Cl(1)	95.4(1)
C(9)-Pd(1)-N(1)	171.6(1)	C(16)-Pd(1)-Cl(1)	171.3(1)
C(16)-Pd(1)-N(1)	97.3(1)	Cl(1)-Pd(1)-N(1)	90.9(1)
O(1)-Ru(1)-P(1)	81.2(1)	O(1)-Ru(1)-Cl(2)	80.7(1)
P(1)-Ru(1)-Cl(2)	88.8(1)	C(9)-P(1)-C(10)	111.2(2)
C(9)-P(1)-C(16)	91.8(1)	C(9)-P(1)-Ru(1)	101.5(1)
C(10)-P(1)-C(16)	110.1(2)	C(10)-P(1)-Ru(1)	118.6 (1)
C(16)-P(1)-Ru(1)	119.4(1)	C(8)-O(1)-Ru(1)	121.1(2)
O(1)-C(8)-C(7)	117.6(3)	O(1)-C(8)-C(9)	122.6(3)
C(7)-C(8)-C(9)	119.7(3)	C(8)-C(9)-P(1)	111.9(2)
C(8)-C(9)-Pd(1)	107.2(2)	P(1)-C(9)-Pd(1)	89.2(1)
C(17)-C(16)-P(1)	128.4(2)	C(17)-C(16)-Pd(1)	135.6(2)
P(1)-C(16)-Pd(1)	94.2(1)	C(16)-C(17)-C(18)	123.1(3)

C(16)-C(17)-C(19)	122.4(3)	C(18)-C(17)-C(19)	114.5(3)
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4.2.1.3 Structural Features of Complex **25**

It is noteworthy that complex **25** has two unusual structural features. Firstly, the 4-membered ring adopts a slightly distorted plane. The ring constraints are responsible for the smaller angles observed. Although the 4-membered rings are not sterically favored, several organometallic complexes bearing similar planar 4-membered rings have been reported.³²⁹⁻³³² Secondly, this molecule is a zwitterionic bimetallic ruthenium(II)-palladium(II) complex containing a formal positive charge at ruthenium and a formal negative charge at palladium. Recently the zwitterionic feature of organotransition metal complexes has been identified as an influential factor in the design of cationic metal catalysts, although only a few examples have been reported.³³³⁻³³⁹

4.2.1.4 Solvent Dependence Studies

The hydration process has also been repeated in several other solvent systems, such as dichloromethane/methanol/water, dichloromethane/acetonitrile/water, and the heterogeneous solvent, dichloromethane/water. However, these conditions resulted in a significant decrease in yield, or rate, or both. Furthermore, in the solvent system of dichloromethane/acetone/water (2/10/1) containing HCl, complex **25** decomposed rapidly.

The yield of the hydration product decreased when more HCl was used. When more than 1 equiv of HCl, all complexes decomposed. In basic solvents, such as the mixture of dichloromethane, acetone, and dilute NaOH solution or the mixture of dichloromethane/acetone/water with 1-2 equiv of Et₃N, the reaction proceeded faster but led to the formation of some unknown compounds and lower yield of the desired product. For those reactions performed in basic solvents, the best yield was obtained from dichloromethane/acetone/water containing 2 equiv of NaOH, in which hydration of complex **23** was completed in 2 days and gave complex **25** in 30% yield.

4.2.1.5 Mechanistic Considerations

The ketonyl product **25** is proposed to form through an enol intermediate, as shown in Scheme 4-4. Aided by palladium, the alkynyl group undergoes the nucleophilic attack by water to generate the complex **27**, which is then converted into the enol intermediate **28** after losing one proton. Complex **28** subsequently undergoes tautomerization to give the ketonyl complex **29**, yielding a stereogenic carbon center at the α -position from phosphorus. Coordination of oxygen to the ruthenium atom followed by loss of one chloride anion gives the ruthenium complex **25**. During this process, one molecule of HCl was formed, which led to the decomposition of some hydration products and thus was responsible for the moderate yield.

Scheme 4-4 (the square indicates the vacant coordination site)

4.2.2 Hydration Reaction of Chiral Insertion Product ($R_{\text{Ru}}R_{\text{P}}S_{\text{C}}$)-**22**, Synthesis of Complex ($R_{\text{Ru}}R_{\text{P}}S_{\text{C}}S_{\text{C}}$)-**30**

Heterobimetallic ruthenium(II)-palladium(II) complex ($R_{\text{Ru}}R_{\text{P}}S_{\text{C}}$)-**22**, underwent the hydration reaction to give the product ($R_{\text{Ru}}R_{\text{P}}S_{\text{C}}S_{\text{C}}$)-**30** (Scheme 4-5). When monitored by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, this reaction was found to be complete in 7 days at room temperature in a mixed solvent system of dichloromethane, acetone, and water (2:10:1). After hydration, in CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture exhibited a singlet at δ 50.0.

Removal of organic solvents under reduced pressure followed by extraction with dichloromethane gave the crude product mixture. This crude mixture was then purified by silica gel column chromatography, and the subsequent precipitation by diethyl ether

gave pure ($R_{Ru}R_P S_C S_C$)-**30** as a yellow solid in 30% yield. Recrystallization of complex ($R_{Ru}R_P S_C S_C$)-**30** from dichloromethane and diethyl ether gave orange prisms. In $CDCl_3$ the $^{31}P\{^1H\}$ NMR spectrum of complex ($R_{Ru}R_P S_C S_C$)-**30** showed a singlet at δ 50.0.

Scheme 4-5

4.2.2.1 X-ray Structural Analysis of Complex ($R_{Ru}R_P S_C S_C$)-**30**

The single crystal X-ray structure of complex ($R_{Ru}R_P S_C S_C$)-**30** is shown in Figure 4-2. The geometry at ruthenium center exhibits the expected and usual "three-legged piano-stool" disposition. The η^6 -coordinated arene is in a "stool" position, while the "legs" comprise P, O, and Cl atoms. The angles at the Ru center are in the range of 81.4(1)-86.1(1)°. Ru(1)-O(1) [2.096(1) Å] has slightly shorter bond length than the other two bonds connecting Ru(1) with P(1) and Cl(2), which have bond lengths of 2.300(1) Å [Ru(1)-P(1)] and 2.378(1) Å [Ru(1)-Cl(2)], respectively. There is a 4-membered ring adopting a slightly distorted planar geometry, which is composed of Pd(1), P(1), C(9), and C(16), in this molecule. The four angles at the vertexes of this 4-membered ring, C(9)-Pd(1)-C(16) [76.3(1)°], P(1)-C(9)-Pd(1) [89.3(1)°], C(9)-P(1)-C(16) [91.1(1)°], and P(1)-C(16)-Pd(1) [94.9(1)°], are distinctly smaller than those observed in normal

geometry and are attributed to the ring constraints. Additionally, the bond length of C(8)-O(1) is 1.259(2) Å, which indicates the generation of a double bond between these two atoms. Therefore a carbonyl group, instead of an enol moiety, has been formed in the product. Moreover, it is interesting to note that the C(8)-C(9) bond length is only 1.434(2) Å, which is shorter than the normal carbon-carbon single bond length. The stereogenic center at C(9) adopts the *S* absolute configuration. The absolute configurations at phosphorus and C(25) remained unchanged after hydration. Selected bond distances and angles for complex (*R*_{Ru}*R*_P*S*_C*S*_C)-**30** are given in Table 4-2.

Figure 4-2 Molecular structure of complex (*R*_{Ru}*R*_P*S*_C*S*_C)-**30**

Table 4-2 Selected Bond Lengths (Å) and Angles (deg) of (*R*_{Ru}*R*_P*S*_C*S*_C)-**30**

Pd(1)-C(9)	2.141(2)	Pd(1)-C(16)	1.993(1)
Pd(1)-N(1)	2.182(2)	Pd(1)-Cl(1)	2.425(1)

Ru(1)-O(1)	2.096(1)	Ru(1)-P(1)	2.300(1)
Ru(1)-Cl(2)	2.378(1)	P(1)-C(9)	1.802(2)
P(1)-C(10)	1.825(2)	P(1)-C(16)	1.778(2)
O(1)-C(8)	1.259(2)	C(8)-C(9)	1.434(2)
C(16)-C(17)	1.340(2)		
C(9)-Pd(1)-C(16)	76.3(1)	C(9)-Pd(1)-Cl(1)	95.8 (1)
C(9)-Pd(1)-N(1)	169.9(1)	C(16)-Pd(1)-Cl(1)	171.9(1)
C(16)-Pd(1)-N(1)	97.4(1)	Cl(1)-Pd(1)-N(1)	90.7(1)
O(1)-Ru(1)-P(1)	81.7(1)	O(1)-Ru(1)-Cl(2)	81.4(1)
P(1)-Ru(1)-Cl(2)	86.1(1)	C(9)-P(1)-C(10)	112.4(1)
C(9)-P(1)-C(16)	91.1(1)	C(9)-P(1)-Ru(1)	101.0(1)
C(10)-P(1)-C(16)	111.2(1)	C(10)-P(1)-Ru(1)	117.5(1)
C(16)-P(1)-Ru(1)	119.6(1)	C(8)-O(1)-Ru(1)	120.9(1)
O(1)-C(8)-C(7)	117.0(2)	O(1)-C(8)-C(9)	122.2(1)
C(7)-C(8)-C(9)	120.8(2)	C(8)-C(9)-P(1)	112.4(1)
C(8)-C(9)-Pd(1)	105.5(1)	P(1)-C(9)-Pd(1)	89.3(1)
C(17)-C(16)-P(1)	130.3(1)	C(17)-C(16)-Pd(1)	133.2(1)
P(1)-C(16)-Pd(1)	94.9(1)	C(16)-C(17)-C(18)	123.4(1)
C(16)-C(17)-C(19)	121.2(1)	C(18)-C(17)-C(19)	115.2(1)

4.2.3 Hydration Reaction of Chiral Insertion Product ($R_{Ru}S_P S_C$)-**22**, Synthesis of Complex ($S_{Ru}S_P R_C S_C$)-**31**

Heterobimetallic ruthenium(II)-palladium(II) ($R_{Ru}S_P S_C$)-**22**, obtained from the insertion reaction, underwent hydration reaction to give the product ($S_{Ru}S_P R_C S_C$)-**31** (Scheme 4-6). When monitored by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, this reaction was found to be complete in 10 days at room temperature in a mixed solvent system of dichloromethane, acetone, and water (2:10:1). After hydration, in CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture exhibited a singlet at δ 49.7.

Scheme 4-6

Removal of organic solvents under reduced pressure followed by extraction with dichloromethane gave the crude mixture. This crude mixture was then purified by silica gel column chromatography, and the subsequent precipitation of the eluted fraction by diethyl ether gave pure ($S_{Ru}S_P R_C S_C$)-**31** as a yellow solid in 13% yield. In CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of ($S_{Ru}S_P R_C S_C$)-**31** showed a singlet at δ 49.7.

4.2.3.1 Absolute Configurations of Complexes ($R_{Ru}R_P S_C S_C$)-**30** and ($S_{Ru}S_P R_C S_C$)-**31**

The structure of ($R_{Ru}R_P S_C S_C$)-**30** was confirmed by X-ray structural analysis, and the structure of ($S_{Ru}S_P R_C S_C$)-**31** was suggested through a Dreiding model study, as shown in Scheme 4-7, and was determined by 2D ROESY NMR studies (See Section 4.2.3.2). The structures of these two complexes are almost mirror-symmetrical except the chiral center at C19 adopting the same *S* absolute configuration, which leads to the generation of the equatorial and axial disposition of Me19 in complexes ($R_{Ru}R_P S_C S_C$)-**30** and ($S_{Ru}S_P R_C S_C$)-**31**, respectively. It is noteworthy that Me19 occupies the sterically unfavored axial position in complex ($S_{Ru}S_P R_C S_C$)-**31**, compared with other complexes bearing the similar structure such as complex ($R_{Ru}R_P S_C S_C$)-**30**, in which the corresponding methyl group is often equatorially disposed to avoid the repulsion with the methyl group on the olefin moiety that corresponds to Me12 in complex ($S_{Ru}S_P R_C S_C$)-**31** (See Section 3.2.1.2).

On the other hand, the absolute configuration at P4 was observed to be retained in each complex. In contrast, after the hydration process, the absolute configuration at ruthenium in complex ($R_{Ru}R_P S_C S_C$)-**30** remained unchanged, while that in complex ($S_{Ru}S_P R_C S_C$)-**31** was reversed. Furthermore, a stereogenic center at C3 has also been formed in these two complexes. The generation of the configurations at Ru and C3 are suggested to be affected by the chirality at P4 (See Section 4.2.1.1).

Scheme 4-7

4.2.3.2 2D ROESY Studies of Complexes ($R_{Ru}R_PSCSC$)-**30** and ($S_{Ru}S_PRCSC$)-**31**

The structures of complexes ($R_{Ru}R_PSCSC$)-**30** and ($S_{Ru}S_PRCSC$)-**31** have been studied through the 2D rotating frame nuclear Overhauser enhancement (ROESY) 1H NMR technique. Scheme 4-7 shows the numbering scheme of these two complexes used in the 2D ROESY NMR analysis. Selected ^{31}P and 1H NMR data of the two products are given in Table 4-3. These NMR assignments are based on a series of 1H , ^{31}P , $^1H\{^{31}P\}$, and 2D ROESY NMR studies. Figures 4-3 and 4-4 show the 2D 1H - 1H ROESY NMR spectra of ($R_{Ru}R_PSCSC$)-**30** and ($S_{Ru}S_PRCSC$)-**31**, respectively.

Figure 4-3. Two-dimensional ^1H ROESY NMR spectrum of $(R_{\text{Ru}}R_{\text{P}}S_{\text{C}}S_{\text{C}})\text{-30}$ in CDCl_3 .

All off-diagonal peaks are of negative intensity. Selected NOE contacts: A, Me19-Me20(ax); B, Me19-Me20(eq); C, Me2-H3; D, Me20(ax)-Me20(eq); E, Me19-H19; F, Me12-H19; G, Me20(eq)-H19; H, H19-C₆H₆; I, Me20(eq)-C₆H₆; J, Me12-C₆H₆; K, Me12-H14; L, Me12-H6,10; M, Me19-H17; N, Me20(ax)-H17; O, H3-H6,10; P, C₆H₆-H6,10.

Figure 4-4. Two-dimensional ^1H ROESY NMR spectrum of $(S_{\text{Ru}}S_{\text{P}}R_{\text{C}}S_{\text{C}})\text{-31}$ in CDCl_3 .

All off-diagonal peaks are of negative intensity except signal O. Selected NOE contacts:

A, Me19-Me20(eq); B, Me19-H19; C, Me2-H3; D, Me20(ax)-Me20(eq); E, H19-Me20(eq); F, H19-Me20(ax); G, Me20(eq)- C_6H_6 ; H, Me12- C_6H_6 ; I, H19-H17; J, Me20(ax)-H17; K, Me12-H14; L, C_6H_6 -H6,10; M, H3-H6,10; N, Me12-H6,10.

Table 4-3. Selected ^{31}P and ^1H NMR Spectra Chemical Shift Values of $(R_{\text{Ru}}R_{\text{P}}S_{\text{C}}S_{\text{C}})$ -30** and $(S_{\text{Ru}}S_{\text{P}}R_{\text{C}}S_{\text{C}})$ -**31** in CDCl_3 (coupling constants in Hz are given in parentheses)**

	$(R_{\text{Ru}}R_{\text{P}}S_{\text{C}}S_{\text{C}})$ - 30	$(S_{\text{Ru}}S_{\text{P}}R_{\text{C}}S_{\text{C}})$ - 31
^{31}P	50.0 s	49.7 s
NCHMe	1.45 d, ($^3J_{\text{HH}} = 7.0$)	1.82 Overlapped with signal of C=C-Me
C=C-Me	1.71 d, ($^4J_{\text{PH}} = 1.8$ Hz)	1.82 Overlapped with signal of NCHMe
O=C-Me	2.35 d, ($^4J_{\text{PH}} = 1.6$ Hz)	2.37 d, ($^4J_{\text{PH}} = 1.7$ Hz)
NMe(ax)	2.50 s	2.68 s
NMe(eq)	3.10 s	2.94 s
PdCH	2.98 s	3.14 s
NCHMe	4.30 q ($^3J_{\text{HH}} = 7.0$)	3.22 q ($^3J_{\text{HH}} = 6.7$)
C ₆ H ₆	5.97 d, ($^3J_{\text{PH}} = 0.9$ Hz)	6.02 d, ($^3J_{\text{PH}} = 0.6$ Hz)
o-PPh	7.55-7.62, m	7.62-7.66, m

The 2D ROESY NMR studies confirmed the absolute configuration at C19 in these two complexes. The 2D ROESY NMR spectrum of $(R_{\text{Ru}}R_{\text{P}}S_{\text{C}}S_{\text{C}})$ -**30** exhibits the clear interactions (A, B) between Me19 and the both two NMe groups (Me20). However, only the equatorial NMe group [Me20(eq)] interacts with H19 (G), while the interaction of H19-Me20(ax) has not been observed. These NOE signals suggest that Me19 is in the

equatorial position in $(R_{Ru}R_P S_C S_C)$ -**30**. Furthermore, a NOE signal of the interaction between Me19 and the neighboring phenyl proton H17 [M, Me19-H17] has been recorded, which is also consistent with the assignment that Me19 is equatorially disposed. In contrast, Me19 in $(S_{Ru}S_P R_C S_C)$ -**31** is in the axial position, according to the results of similar NMR studies. The 2D ROESY NMR spectrum of $(S_{Ru}S_P R_C S_C)$ -**31** clearly shows the interactions of H19-Me20(eq) (E), H19-Me20(ax) (F), and Me19-Me20(eq) (A). There is no signal resulting from the interaction between Me19 and Me20(ax). Moreover, H19, rather than Me19, is also observed to interact with H17, producing signal I (H19-H17). These signals indicate that Me19 is axially disposed in complex $(S_{Ru}S_P R_C S_C)$ -**31**.

The 2D ROESY NMR studies also indicate that the interactions involving η^6 -benzene ligand, the PPh group, the NMe groups, and the axial group on C19 are similar in complexes $(R_{Ru}R_P S_C S_C)$ -**30** and $(S_{Ru}S_P R_C S_C)$ -**31**. The 2D ROESY NMR spectrum of complex $(R_{Ru}R_P S_C S_C)$ -**30** shows the signals of C₆H₆-H19 (H) and C₆H₆-Me20(eq) (I), while no interactions of H6, 10-H19 and H6, 10-Me20(eq) have been found. This information indicates that η^6 -benzene, rather than PPh, is close to the NMe groups and C19, and thus allows the assignment of the *R* absolute configuration at phosphorus in complex $(R_{Ru}R_P S_C S_C)$ -**30**. In the case of complex $(S_{Ru}S_P R_C S_C)$ -**31**, it is not clear whether signals H and N include the NOE interactions of C₆H₆-Me19 and H6, 10-Me19, respectively, due to the overlap of Me12 and Me19 resonance in the ¹H NMR spectrum. However, signal G [C₆H₆-Me20(eq)] and the absence of the interaction of H6, 10-Me20(eq) suggest the proximity between η^6 -benzene and NMe groups. The signal is

consistent with the *S* absolute configuration at phosphorus in complex (*S*_{Ru}*S*_P*R*_C*S*_C)-**31**. Additionally, other similar signals in these two 2D ROESY NMR spectra are also observed. Me12 is observed to interact with the neighboring aromatic proton H14 (K in both spectra) and o-PPh (H6,10) [L in case of (*R*_{Ru}*R*_P*S*_C*S*_C)-**30** and N in case of (*S*_{Ru}*S*_P*R*_C*S*_C)-**31**, respectively]. The interactions of H3-Me2 (C in both spectra) and H3-o-PPh (H6,10) [O in case of (*R*_{Ru}*R*_P*S*_C*S*_C)-**30** and M in case of (*S*_{Ru}*S*_P*R*_C*S*_C)-**31**] have also been found in both ROESY spectra due to their closeness.

These signals in the 2D ROESY NMR spectra are consistent with the X-ray structure of complex (*R*_{Ru}*R*_P*S*_C*S*_C)-**30** and the interactions expected from the structures of both complexes in Scheme 4-7, thus confirming their configurations in solution.

4.2.3.3 Reactivities of Hydration Reactions to Generate Complexes (*R*_{Ru}*R*_P*S*_C*S*_C)-**30** and (*S*_{Ru}*S*_P*R*_C*S*_C)-**31**

The hydration reaction of complex (*R*_{Ru}*R*_P*S*_C)-**22** was completed in 7 days and generated (*R*_{Ru}*R*_P*S*_C*S*_C)-**30** in 30% yield in a mixed solvent system of dichloromethane, acetone, and water (2:10:1) at room temperature. The hydration reaction of complex (*R*_{Ru}*S*_P*S*_C)-**22** was observed to be complete in 10 days and generated (*S*_{Ru}*S*_P*R*_C*S*_C)-**31** in only 13% yield under similar conditions. The longer reaction time and the lower yield indicate that complex (*R*_{Ru}*S*_P*S*_C)-**22** is less reactive toward hydration than that of (*R*_{Ru}*R*_P*S*_C)-**22**. The possible reason is that the product (*S*_{Ru}*S*_P*R*_C*S*_C)-**31** is sterically less favored when compared with complex (*R*_{Ru}*R*_P*S*_C*S*_C)-**30**. In complex (*S*_{Ru}*S*_P*R*_C*S*_C)-**31**,

Me19 is in the axial position, as shown in Scheme 4-7, thus generating the repulsion with Me12. In ($R_{Ru}R_P S_C S_C$)-**30**, Me19 occupies the equatorial position that is sterically favored due to lack of undesirable repulsion.

4.3 Conclusions

The hydration reactions of complexes ($R_{Ru}R_P S_C$)-**22**, ($R_{Ru}S_P S_C$)-**22**, and **23** were carried out at room temperature. This process converted the alkyne moiety into a ketonyl group, which coordinated to ruthenium through oxygen, thus generating bifunctionalized phosphine complexes. It is noteworthy that the absolute configuration at phosphorus remained unchanged in those products. The newly formed bifunctionalized phosphine also bonds to palladium via the two carbon atoms at the α -position from phosphorus, which results in the generation of an unusual Pd-C-P-C 4-membered ring adopting a slightly distorted planar geometry. Many solvent systems used in this hydration reaction have been scanned and the moderate reaction rates and yields were obtained by using the mixed solvent system of dichloromethane, acetone, and water (2:10:1). Moreover, it is interesting to note that the hydration products are zwitterionic bimetallic complexes, which bear an anionic palladium and a cationic ruthenium centers.

4.4 Experimental

Synthesis of Complex **25**

Complex **23** (0.042 g, 0.058 mmol) was stirred in a mixed solvent system (dichloromethane, 1 mL; Acetone, 5 mL; and water, 0.5 mL) for 5 days. Removal of organic solvents through rotatory evaporation followed by extraction with dichloromethane gave the crude mixture. The crude mixture was then purified by silica gel column chromatography (acetone-dichloromethane, 1:4), and the subsequent precipitation by diethyl ether gave **25** as a yellow solid. Yield: 0.014 g (34%). Complex **25** was recrystallized from dichloromethane and diethyl ether as orange prisms, which were suitable for X-ray analysis. Mp: 240-241 °C dec. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 49.8 (s). ^1H NMR (CDCl_3 , δ): 1.71 (d, $^4J_{\text{PH}} = 1.4$ Hz, 3H, C=C-Me); 2.36 (d, $^4J_{\text{PH}} = 1.3$ Hz, 3H, O=C-Me); 2.49 (s, 3H, NMe); 3.00-3.04 (m, 4H, PCH and NMe); 3.24 ($^2J_{\text{HH}} = 11.0$ Hz, 1H), 3.99 ($^2J_{\text{HH}} = 11.0$ Hz, 1H) (d, NCHH); 5.95 (s, 6H, C_6H_6); 7.15-7.23 (3H), 7.31-7.44 (4H), 7.59-7.65 (2H) (m, aromatics). Anal. Calcd for $\text{C}_{27}\text{H}_{30}\text{Cl}_2\text{NOPpRu}\cdot\text{H}_2\text{O}$: C, 45.6; H, 4.5; N, 2.0. Found: C, 45.6; H, 4.5; N, 2.0.

Synthesis of Complex ($R_{\text{Ru}}R_{\text{P}}S_{\text{C}}S_{\text{C}}$)-**30**

Complex ($R_{\text{Ru}}R_{\text{P}}S_{\text{C}}$)-**22** (0.041 g, 0.057 mmol) was stirred in a mixed solvent system (dichloromethane, 1 mL; Acetone, 5 mL; and water, 0.5 mL) for 7 days. Removal of organic solvents through rotatory evaporation followed by extraction with dichloromethane gave the crude mixture. The crude mixture was then purified by silica gel column chromatography (acetone-dichloromethane, 1:4), and the subsequent precipitation by diethyl ether gave ($R_{\text{Ru}}R_{\text{P}}S_{\text{C}}S_{\text{C}}$)-**30** as a yellow solid. Yield: 0.012 g (30%). Complex ($R_{\text{Ru}}R_{\text{P}}S_{\text{C}}S_{\text{C}}$)-**30** was recrystallized from dichloromethane and diethyl

ether as orange prisms, which were suitable for X-ray analysis. Mp: 235-236 °C dec. $[\alpha]_D$ -30.0° (*c* 0.5, CHCl₃). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃, δ): 50.0 (s). ^1H NMR (CDCl₃, δ): 1.45 (d, $^3J_{\text{HH}} = 7.0$ Hz, 3H, NCHMe); 1.71 (d, $^4J_{\text{PH}} = 1.8$ Hz, 3H, C=C-Me); 2.35 (d, $^4J_{\text{PH}} = 1.6$ Hz, 3H, O=C-Me); 2.50 (s, 3H, NMe); 2.98 (s, 1H, PCH); 3.10 (s, 3H, NMe); 4.30 (q, $^3J_{\text{HH}} = 7.0$ Hz, 1H, NCHMe); 5.97 (d, $^3J_{\text{PH}} = 0.9$ Hz, 6H, C₆H₆); 7.10-7.13 (1H), 7.22-7.33 (3H), 7.35-7.45 (3H), 7.55-7.62 (2H) (m, aromatics). Anal. Calcd for C₂₈H₃₂Cl₂NOPPdRu·H₂O: C, 46.3; H, 4.7; N, 1.9. Found: C, 46.1; H, 4.7; N, 2.0.

Synthesis of Complex (*S*_{Ru}*S*_P*R*_C*S*_C)-**31**

Complex (*R*_{Ru}*S*_P*S*_C)-**22** (0.065 g, 0.090 mmol) was stirred in a mixed solvent system (dichloromethane, 1.5 mL; Acetone, 7.5 mL; and water, 0.8 mL) for 10 days. Removal of organic solvents through rotatory evaporation followed by extraction with dichloromethane gave the crude mixture. The crude mixture was then purified by silica gel column chromatography (acetone-dichloromethane, 1:4), and the subsequent precipitation by diethyl ether gave (*S*_{Ru}*S*_P*R*_C*S*_C)-**31** as a yellow solid. Yield: 0.008 g (13%). Mp: 236-237 °C dec. $[\alpha]_D$ +56.7° (*c* 0.6, CHCl₃). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃, δ): 49.7 (s). ^1H NMR (CDCl₃, δ): 1.81-1.83 (m, 6H, NCHMe and C=C-Me); 2.37 (d, $^4J_{\text{PH}} = 1.7$ Hz, 3H, O=C-Me); 2.68 (s, 3H, NMe); 2.94 (s, 3H, NMe); 3.14 (s, 1H, PCH); 3.22 (q, $^3J_{\text{HH}} = 6.7$ Hz, 1H, NCHMe); 6.02 (d, $^3J_{\text{PH}} = 0.6$ Hz, 6H, C₆H₆); 7.03-7.04 (1H), 7.09-7.10 (1H), 7.15-7.18 (1H), 7.25-7.28 (1H), 7.34-7.43 (3H), 7.62-7.66 (2H) (m, aromatics). Anal. Calcd for C₂₈H₃₂Cl₂NOPPdRu: C, 47.5; H, 4.6; N, 2.0. Found: C, 47.1; H, 4.5; N, 1.9.

Chapter 5

Hydroamination Reactions of the Bimetallic Ruthenium(II)-Palladium(II) Complexes Bearing a Free Alkyne Moiety

5.1 Introduction

A formal addition of an N-H bond across carbon-carbon unsaturated bonds, collectively known as hydroamination, has received considerable attention as a simple and atom-economical protocol for N-functionalization. Hydroamination of alkynes, as a fundamental reaction in organic synthesis, allows the generation of valuable nitrogen-containing compounds such as enamines and imines in a straightforward manner. Since the high activation energy is required for this process, a variety of catalytic and noncatalytic methods, such as thermal-, acid-, base-promoted, and transition metal-catalyzed reactions,²⁷⁹ have been developed. Both intra and intermolecular hydroaminations have been reported. For intramolecular hydroamination, tethered aminoalkynes have been reported to be cyclized using titanium,³⁴⁰ nickel,²⁸⁰ palladium,²⁸² gold,²⁸¹ and lanthanide^{283, 284} complexes as catalysts. These processes are capable of regiospecifically forming five-, six-, and seven-membered heterocycles from substrates bearing various substituents such as H, alkyl, Ph, SiMe₃, and allyl groups on the alkyne moiety. Cyclization rates are influenced considerably by the involved substituents and show a strong ring size dependence with 5 > 6 >> 7.^{283, 284} Furthermore,

intermolecular hydroamination of alkynes could proceed through Markovnikov and *anti*-Markovnikov pathways, when catalyzed by transition metal complexes. For example, the Ti complexes with amine ligands often catalyzed the hydroamination of terminal alkynes in Markovnikov manner,²⁸⁵⁻²⁸⁸ while those with Cp and amidate ligands was observed to promote similar reactions to give *anti*-Markovnikov products.²⁸⁹⁻²⁹³ The late transition metal complexes such as $\text{Ru}_3(\text{CO})_{12}$ ²⁹⁵ and $[\text{Rh}(\text{COD})_2]\text{BF}_4$ ²⁹⁶ have also been reported to catalyze the hydroamination reactions of terminal alkynes with a Markovnikov regiochemistry.

In this chapter, the addition of a variety of amines to the alkyne moiety of the bimetallic ruthenium(II)-palladium(II) complexes, which were prepared through the insertions in Chapter 3, has been studied. These reactions converted the carbon-carbon triple bond into an imino group under mild conditions, thus generating bifunctionalized phosphine complexes. Furthermore, the newly generated imino group is always found to bond to the carbon β to phosphorus regioselectively. Like the hydration reactions in Chapter 4, the hydroamination reactions also generated an unusual Pd-C-P-C 4-membered ring adopting a slightly distorted planar geometry in those products, which was identified by X-ray crystallographic analysis. Additionally, the hydroamination products are zwitterionic bimetallic ruthenium(II)-palladium(II) complexes, which have a positive charge at the protonized imine moiety and a negative charge at palladium.

5.2 Results and Discussion

5.2.1 Hydroamination Reactions Involving Aniline

Addition of aniline to the insertion products **23**, $(R_{Ru}R_P S_C)\text{-}\mathbf{22}$, and $(R_{Ru}S_P S_C)\text{-}\mathbf{22}$ have been studied. These reactions were carried out in dichloromethane at room temperature. After the hydroamination was completed, as indicated by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, the crude reaction mixture was then purified by silica gel column chromatography and subsequently precipitated by diethyl ether or hexane to give the corresponding products.

When monitored by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, the reaction of complex **23** and aniline was found to be complete in 1.5 days. The resulting reaction mixture exhibited a broad singlet at δ 41.0 in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CDCl_3). Silica gel column chromatography and the subsequent precipitation by diethyl ether gave **32** as a yellow solid in 57% yield. Recrystallization of complex **32** from dichloromethane and diethyl ether gave red prisms. In CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **32** showed a broad

singlet at δ 41.0 (Scheme 5-1).

Scheme 5-1

Interestingly the reaction of complex (*R*_{Ru}*R*_P*S*_C)-**22** and aniline did not give the desired product. However, the reaction of the corresponding diastereomeric complex (*R*_{Ru}*S*_P*S*_C)-**22** and aniline gave the hydroamination product (*S*_P*R*_C*S*_C)-**33** in high yield (Scheme 5-2). When monitored by the ³¹P{¹H} NMR spectroscopy, the reaction of complex (*R*_{Ru}*S*_P*S*_C)-**22** and aniline was found to be complete in 1.5 days. The resulting reaction mixture exhibited a broad singlet at δ 41.3 in the ³¹P{¹H} NMR spectrum (CDCl₃). Silica gel column chromatography and the subsequent precipitation by hexane gave (*S*_P*R*_C*S*_C)-**33** as a yellow solid in 64% yield. In CDCl₃ the ³¹P{¹H} NMR spectrum of (*S*_P*R*_C*S*_C)-**33** showed a broad singlet at δ 41.3.

Scheme 5-2

5.2.1.1 X-ray Structural Analysis of Complex 32

The single crystal X-ray structure of complex **32** is shown in Figure 5-1. A pair of enantiomers exist in a ratio of 1:1 in each unit cell. The geometry at ruthenium center exhibits the expected and usual "three-legged piano-stool" disposition. The η^6 -coordinated arene is in a "stool" position, while the "legs" comprise P and Cl atoms. The angles at the Ru center are in the range of 87.4(1)-88.8(1)°. There is a 4-membered ring adopting a slightly distorted planar geometry, which is composed of Pd(1), P(1), C(13), and C(22), in this molecule. The four angles at the vertexes of this 4-membered ring, C(13)-Pd(1)-C(22) [76.6(1)°], P(1)-C(13)-Pd(1) [90.0(1)°], C(13)-P(1)-C(22) [89.5(1)°], and P(1)-C(22)-Pd(1) [93.9(1)°], are distinctly smaller than those observed in normal geometry, which is attributed to the ring constraints. Additionally, the bond length of C(14)-N(1) is 1.325(3) Å, which indicates the generation of a double bond between

these two atoms. Therefore an imine, instead of an enamine, has been formed in the product. It is noteworthy that the C(13)-C(14) bond length is only 1.419(3) Å, which is shorter than the normal single carbon-carbon bond length. The absolute configuration of the structure shown in Figure 5-1 is designated as R_pS_C , while its enantiomer adopts the S_pR_C absolute configuration. Selected bond distances and angles for complex **32** are given in Table 5-1.

Figure 5-1. Molecular structure of complex **32**.

Table 5-1. Selected Bond Lengths (Å) and Angles (deg) of **32**

Ru(1)-P(1)	2.363(1)	Ru(1)-Cl(1)	2.411(1)
Ru(1)-Cl(2)	2.417(1)	P(1)-C(7)	1.834(2)
P(1)-C(13)	1.821(2)	P(1)-C(22)	1.813(2)
Pd(1)-C(13)	2.120(2)	Pd(1)-C(22)	2.006(2)

Pd(1)-N(2)	2.142(2)	Pd(1)-Cl(3)	2.413(1)
C(22)-C(23)	1.333(3)	C(13)-C(14)	1.419(3)
C(14)-N(1)	1.325(3)		
P(1)-Ru(1)-Cl(1)	88.6 (1)	P(1)-Ru(1)-Cl(2)	88.8(1)
Cl(1)-Ru(1)-Cl(2)	87.4(1)	C(7)-P(1)-Ru(1)	112.9(1)
C(13)-P(1)-Ru(1)	118.5(1)	C(22)-P(1)-Ru(1)	128.4(1)
C(7)-P(1)-C(13)	100.7(1)	C(7)-P(1)-C(22)	101.7(1)
C(13)-P(1)-C(22)	89.5(1)	C(13)-Pd(1)-C(22)	76.6(1)
C(13)-Pd(1)-N(2)	166.7(1)	C(13)-Pd(1)-Cl(3)	94.5(1)
C(22)-Pd(1)-N(2)	97.2(1)	C(22)-Pd(1)-Cl(3)	171.1(1)
N(2)-Pd(1)-Cl(3)	91.4(1)	C(14)-C(13)-P(1)	123.4(2)
C(14)-C(13)-Pd(1)	98.2(1)	P(1)-C(13)-Pd(1)	90.0(1)
C(23)-C(22)-P(1)	130.5(2)	C(23)-C(22)-Pd(1)	135.3(2)
P(1)-C(22)-Pd(1)	93.9(1)	N(1)-C(14)-C(13)	122.7(2)
N(1)-C(14)-C(15)	119.0(2)	C(13)-C(14)-C(15)	118.2(2)
C(14)-N(1)-C(16)	127.0(2)		

5.2.1.2 2D ROESY Studies of Complex ($S_pR_C S_C$)-33

The structure of ($S_pR_C S_C$)-33 has been studied through the 2D rotating frame nuclear Overhauser enhancement (ROESY) ^1H NMR technique. Scheme 5-3 shows the

numbering scheme of (*S_PR_CS_C*)-**33** used in the 2D ROESY NMR analysis. Selected ^{31}P and ^1H NMR data of (*S_PR_CS_C*)-**33** is given in Table 5-2. These NMR assignments are based on a series of ^1H , ^{31}P , $^1\text{H}\{^{31}\text{P}\}$, and 2D ROESY NMR studies. Figure 5-2 shows the 2D ^1H - ^1H ROESY NMR spectrum of (*S_PR_CS_C*)-**33**.

Scheme 5-3

Table 5-2. Selected ^{31}P and ^1H NMR Spectra Chemical Shift Values of (*S_PR_CS_C*)-33** in CDCl_3 (coupling constants in Hz are given in parentheses)**

<i>(S_PR_CS_C)-33</i>	
^{31}P	41.3 s. br.
NCH <i>Me</i>	1.40 d, ($^3J_{\text{HH}} = 7.0$)
N=C- <i>Me</i>	2.22 s
C=C- <i>Me</i>	2.43 Overlapped with signal of N <i>Me(ax)</i>
N <i>Me(ax)</i>	2.43 Overlapped with signal of C=C- <i>Me</i>

NMe(eq)	2.66 s
PdCH	3.22 d ($^2J_{\text{PH}} = 5.4$)
NCHMe	4.26 q ($^3J_{\text{HH}} = 7.0$)
C ₆ H ₆	5.22 s
o-PPh	7.88-7.94, m

Figure 5-2. Two-dimensional ^1H ROESY NMR spectrum of complex ($S_{\text{P}}R_{\text{C}}S_{\text{C}}$)-**33** in CDCl_3 . All off-diagonal peaks are of negative intensity. Selected NOE contacts: A, Me16-Me17(ax); B, Me16-Me17(eq); C, Me19-H18; D, Me16-H16; E, Me17(eq)-H16; F,

Me9-H16; G, C₆H₆-Me9; H, Me16-H13; I, Me16-H14; J, Me19-H22,26; K, Me9-H11; L, Me17(ax)-H13; M, Me17(ax)-H14; N, C₆H₆-H3,5; O, C₆H₆-H2,6; P, H16-H2,6; Q, H18-H2,6; R, Me17(eq)-H2,6; S, Me9-H2,6; T, H20-H22,26.

Through a Dreiding model study, the possible structure of complex (*S_PR_CS_C*)-**33** is shown in Scheme 5-3. The proposed structure is consistent with the signals observed in the 2D ROESY NMR spectrum. Present in the spectrum, the interactions (A, B) between Me16 and the two NMe(Me17) groups are clear. For the two NMe groups, only the equatorial NMe [Me17(eq)], rather than the axial NMe [Me17(ax)], interacts with H16 (E). These signals resulting from the interactions involving Me17, Me16, and H16 reflects that Me16 occupies the equatorial position. On the other hand, there are clear signals due to the interactions between o-PPh(H2,6) and H16 (P, H16-H2,6), Me17(eq) [R, Me17(eq)-H2,6], respectively, in this spectrum. In contrast, the interaction between the coordinated benzene and Me17 or H16 is not observed due to the long distances. These interactions involving the coordinated benzene, the PPh group, the NMe groups, and H16 indicates that the phosphorus atom adopts the *S* absolute configuration, which remained unchanged after hydroamination. Additionally, H18, rather than Me19 or H20, interacts with PPh(H2,6) (Q), which suggests that H18 is *syn* to the PPh group, allowing the assignment of the absolute *R* configuration at C18.

5.2.2 Hydroamination Reactions Involving Benzylamine

Addition of benzylamine to the insertion product **23** has been studied. When

monitored by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, this reaction was found to be complete in 2 days at room temperature in dichloromethane. After hydroamination, in CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture exhibited a broad singlet at δ 42.2. The crude mixture was then purified by silica gel column chromatography and subsequently precipitated by diethyl ether to give the product **34** as a yellow solid in 36% yield (Scheme 5-3). Recrystallization of complex **34** from dichloromethane and diethyl ether gave red prisms. In CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **34** showed a broad singlet at δ 42.2.

Scheme 5-3

5.2.2.1 X-ray Structural Analysis of Complex **34**

The single crystal X-ray structure of complex **34** is shown in Figure 5-3. A pair of enantiomers exists with a ratio of 1:1 in each unit cell. The geometry at ruthenium center exhibits the expected and usual "three-legged piano-stool" disposition. The η^6 -coordinated arene is in a "stool" position, while the "legs" comprise P and Cl atoms. The angles at the Ru center are in the range of $85.2(1)$ - $89.2(1)^\circ$. There is a 4-membered ring adopting a slightly distorted planar geometry, which is composed of $\text{Pd}(1)$, $\text{P}(1)$,

C(13), and C(23), in this molecule. The four angles at the vertices of this 4-membered ring, C(13)-Pd(1)-C(23) [76.6(3)°], P(1)-C(13)-Pd(1) [89.7(3)°], C(13)-P(1)-C(23) [89.5(3)°], and P(1)-C(23)-Pd(1) [94.2(3)°], are distinctly smaller than those observed in normal geometry, which is attributed to the ring constraints. Additionally, the bond length of C(14)-N(2) is 1.314(9) Å, which indicates the generation of a double bond between these two atoms. Therefore an imine, instead of an enamine, has been formed in the product. It is noteworthy that the C(13)-C(14) bond length is only 1.428(9) Å, which is shorter than the normal single carbon-carbon bond length. The absolute configuration of the structure shown in Figure 5-1 is designated as $S_P R_C$, while its enantiomer adopts the $R_P S_C$ absolute configuration. Selected bond distances and angles for complex **34** are given in Table 5-3.

Figure 5-3. Molecular structure of complex **34**.

Table 5-3. Selected Bond Lengths (Å) and Angles (deg) of **34**

Ru(1)-P(1)	2.364(2)	Ru(1)-Cl(1)	2.391(2)
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Ru(1)-Cl(2)	2.430(2)	P(1)-C(7)	1.826(6)
P(1)-C(13)	1.825(7)	P(1)-C(23)	1.801(7)
Pd(1)-C(13)	2.117(6)	Pd(1)-C(23)	2.000(6)
Pd(1)-N(1)	2.145(5)	Pd(1)-Cl(3)	2.431(2)
C(23)-C(24)	1.330(9)	C(13)-C(14)	1.428(9)
C(14)-N(2)	1.314(9)		
P(1)-Ru(1)-Cl(1)	85.2(1)	P(1)-Ru(1)-Cl(2)	88.8(1)
Cl(1)-Ru(1)-Cl(2)	89.2(1)	C(7)-P(1)-Ru(1)	109.1(2)
C(13)-P(1)-Ru(1)	121.9(2)	C(23)-P(1)-Ru(1)	127.2(2)
C(7)-P(1)-C(13)	100.0(3)	C(7)-P(1)-C(23)	104.8(3)
C(13)-P(1)-C(23)	89.5(3)	C(13)-Pd(1)-C(23)	76.6(3)
C(13)-Pd(1)-N(1)	168.2(2)	C(13)-Pd(1)-Cl(3)	95.0(2)
C(23)-Pd(1)-N(1)	97.1(2)	C(23)-Pd(1)-Cl(3)	171.3(2)
N(1)-Pd(1)-Cl(3)	90.8(2)	C(14)-C(13)-P(1)	125.4(5)
C(14)-C(13)-Pd(1)	102.7(4)	P(1)-C(13)-Pd(1)	89.7(3)
C(24)-C(23)-P(1)	130.0(5)	C(24)-C(23)-Pd(1)	135.4(5)
P(1)-C(23)-Pd(1)	94.2(3)	N(2)-C(14)-C(13)	122.1(6)
N(2)-C(14)-C(15)	119.9(6)	C(13)-C(14)-C(15)	118.0(6)
C(14)-N(2)-C(16)	125.6(6)		

5.2.3 Hydroamination Reactions Involving 2-Phenylethylamine

When monitored by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, the addition of 2-phenylethylamine to complex **23** was found to be complete in 2 days at room temperature in dichloromethane. After hydroamination, in CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture exhibited a broad singlet at δ 42.6. The crude mixture was then purified by silica gel column chromatography and subsequently precipitated by hexane to give the product **35** as a yellow solid in 36% yield (Scheme 5-4). In CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **35** showed a broad singlet at δ 42.6.

Scheme 5-4

5.2.4 Hydroamination Reactions Involving *n*-Butylamine

Additions of *n*-butylamine to the insertion products **23**, ($R_{\text{Ru}}R_{\text{P}}S_{\text{C}}$)-**22**, and ($R_{\text{Ru}}S_{\text{P}}S_{\text{C}}$)-**22** have been studied. The reaction was carried out in dichloromethane at room temperature. After the reaction was completed, as indicated by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, the crude reaction mixture was then purified by silica gel column chromatography and subsequently precipitated by diethyl ether or hexane to give the corresponding products.

When monitored by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, the reaction of complex **23** and 3 equiv of. *n*-butylamine was found to be complete in 1 day. The resulting reaction mixture exhibited a broad singlet at δ 43.1 in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CDCl_3). Silica gel column chromatography and the subsequent precipitation by hexane gave **36** as an orange solid in 28% yield (Scheme 5-5). Recrystallization of complex **36** from dichloromethane and diethyl ether gave red prisms. In CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **36** showed a broad singlet at δ 43.1.

Scheme 5-5

The reaction of complex ($R_{\text{Ru}}R_{\text{P}}S_{\text{C}}$)-**22** and *n*-butylamine gave the hydroamination product ($R_{\text{P}}S_{\text{C}}S_{\text{C}}$)-**37** in similar yield. When monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, the reaction of complex ($R_{\text{Ru}}R_{\text{P}}S_{\text{C}}$)-**22** and 2 equiv of. *n*-butylamine was found to be complete in 1 day. The resulting reaction mixture exhibited a broad singlet at δ 44.3 in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CDCl_3). Silica gel column chromatography and the subsequent precipitation by hexane gave ($R_{\text{P}}S_{\text{C}}S_{\text{C}}$)-**37** as a yellow-orange solid in 25% yield (Scheme 5-6). Recrystallization of complex ($R_{\text{P}}S_{\text{C}}S_{\text{C}}$)-**37** from dichloromethane and diethyl ether gave red needles. In CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of ($R_{\text{P}}S_{\text{C}}S_{\text{C}}$)-**37**

showed a broad singlet at δ 44.3.

On the other hand, the reaction of complex $(R_{Ru}S_PSC)$ -**22** and *n*-butylamine gave the hydroamination product (S_PRCSC) -**38** in similar yield. When monitored by the $^{31}P\{^1H\}$ NMR spectroscopy, the reaction of complex $(R_{Ru}S_PSC)$ -**22** and 2 equiv. of *n*-butylamine was found to be complete in 1 day. The resulting reaction mixture exhibited a broad singlet at δ 43.9 in the $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$). Silica gel column chromatography and the subsequent precipitation by hexane gave (S_PRCSC) -**38** as an orange solid in 18% yield (Scheme 5-7). In $CDCl_3$ the $^{31}P\{^1H\}$ NMR spectrum of (S_PRCSC) -**38** showed a broad singlet at δ 43.9.

5.2.4.1 X-ray Structural Analysis of Complex 36

The single crystal X-ray structure of complex **36** is shown in Figure 5-4. A pair of enantiomers exists with a ratio of 1:1 in each unit cell. The geometry at ruthenium center exhibits the expected and usual "three-legged piano-stool" disposition. The η^6 -coordinated arene is in a "stool" position, while the "legs" comprise P and Cl atoms. The angles at the Ru center are in the range of 83.7(1)-90.0(1)°. There is a 4-membered ring adopting a slightly distorted planar geometry, which is composed of Pd(1), P(1), C(13), and C(25), in this molecule. The four angles at the vertices of this 4-membered ring, C(13)-Pd(1)-C(25) [77.0(1)°], P(1)-C(13)-Pd(1) [93.2(2)°], C(13)-P(1)-C(25) [89.4(2)°], and P(1)-C(25)-Pd(1) [89.0(2)°], are distinctly smaller than those observed in normal geometry, which is attributed to the ring constraints. Additionally, the bond length of C(26)-N(1) is 1.324(6) Å, which indicates the generation of a double bond between these two atoms. Therefore an imine, instead of an enamine, has been formed in the product. It is noteworthy that the C(25)-C(26) bond length is only 1.418(6) Å, which is shorter than the normal single carbon-carbon bond length. The absolute configuration of the structure shown in Figure 5-4 is designated as R_pS_C , while its enantiomer adopts the S_pR_C absolute configuration. Selected bond distances and angles for complex **36** are given in Table 5-4.

Figure 5-4. Molecular structure of complex **36**.

Table 5-4. Selected Bond Lengths (Å) and Angles (deg) of **36**

Ru(1)-P(1)	2.356(1)	Ru(1)-Cl(1)	2.425(1)
Ru(1)-Cl(2)	2.410(1)	P(1)-C(7)	1.822(4)
P(1)-C(13)	1.808(4)	P(1)-C(25)	1.827(4)
Pd(1)-C(13)	1.996(4)	Pd(1)-C(25)	2.110(4)
Pd(1)-N(2)	2.154(4)	Pd(1)-Cl(3)	2.411(1)
C(13)-C(14)	1.338(5)	C(25)-C(26)	1.418(6)
C(26)-N(1)	1.324(6)		
P(1)-Ru(1)-Cl(1)	88.4(1)	P(1)-Ru(1)-Cl(2)	83.7(1)
Cl(1)-Ru(1)-Cl(2)	90.0(1)	C(7)-P(1)-Ru(1)	107.9(1)
C(13)-P(1)-Ru(1)	130.3(1)	C(25)-P(1)-Ru(1)	122.6(1)
C(7)-P(1)-C(13)	102.0(2)	C(7)-P(1)-C(25)	99.4(2)

C(13)-P(1)-C(25)	89.4(2)	C(13)-Pd(1)-C(25)	77.0(1)
C(13)-Pd(1)-N(2)	97.1(2)	C(13)-Pd(1)-Cl(3)	172.2(1)
C(25)-Pd(1)-N(2)	165.2(2)	C(25)-Pd(1)-Cl(3)	95.3(1)
N(2)-Pd(1)-Cl(3)	90.2(1)	C(14)-C(13)-P(1)	131.5(3)
C(14)-C(13)-Pd(1)	134.5(3)	P(1)-C(13)-Pd(1)	93.2(2)
C(26)-C(25)-P(1)	126.2(3)	C(26)-C(25)-Pd(1)	106.4(3)
P(1)-C(25)-Pd(1)	89.0(2)	N(1)-C(26)-C(25)	123.7(4)
N(1)-C(26)-C(27)	119.0(4)	C(25)-C(26)-C(27)	117.2(4)
C(26)-N(1)-C(28)	127.6(4)		

5.2.4.2 X-ray Structural Analysis of Complex ($R_pS_C S_C$)-**37**

The single crystal X-ray structure of complex ($R_pS_C S_C$)-**37** is shown in Figure 5-5. The geometry at ruthenium center exhibits the expected and usual "three-legged piano-stool" disposition. The η^6 -coordinated arene is in a "stool" position, while the "legs" comprise P and Cl atoms. The angles at the Ru center are in the range of 86.2(1)-89.8(1)°. There is a 4-membered ring adopting a slightly distorted planar geometry, which is composed of Pd(1), P(1), C(13), and C(20), in this molecule. The four angles at the vertexes of this 4-membered ring, C(13)-Pd(1)-C(20) [76.8(1)°], P(1)-C(13)-Pd(1) [91.5(1)°], C(13)-P(1)-C(20) [89.3(1)°], and P(1)-C(20)-Pd(1) [95.2(1)°], are distinctly smaller than those observed in normal geometry, which is attributed to the ring constrains. Additionally, the bond length of C(14)-N(1) is 1.298(4)

Å, which indicates the generation of a double bond between these two atoms. Therefore an imine, instead of an enamine, has been formed in the product. It is noteworthy that the C(13)-C(14) bond length is only 1.426(4) Å, which is shorter than the normal single carbon-carbon bond length. Furthermore, C29 adopts the *S* absolute configuration, which remained unchanged after hydroamination. It should be noted that the methyl group C30, stemming from the chiral carbon atom of the 7-membered ring, occupies the unusual axial position, as it would be expected to generate the unfavourable steric interaction between C30 and Me22 in this structure. Selected bond distances and angles for complex (*R_pS_CS_C*)-**37** are given in Table 5-5.

Figure 5-5. Molecular structure of complex (*R_pS_CS_C*)-**37**.

Table 5-5. Selected Bond Lengths (Å) and Angles (deg) of (*R_pS_CS_C*)-**37**

Ru(1)-P(1)	2.371(1)	Ru(1)-Cl(1)	2.399(1)
Ru(1)-Cl(2)	2.427(1)	P(1)-C(7)	1.827(3)

P(1)-C(13)	1.823(3)	P(1)-C(20)	1.801(3)
Pd(1)-C(13)	2.095(3)	Pd(1)-C(20)	2.002(3)
Pd(1)-N(2)	2.162(3)	Pd(1)-Cl(3)	2.430(1)
C(20)-C(21)	1.333(4)	C(13)-C(14)	1.426(4)
C(14)-N(1)	1.298(4)		
P(1)-Ru(1)-Cl(1)	86.2(1)	P(1)-Ru(1)-Cl(2)	88.7(1)
Cl(1)-Ru(1)-Cl(2)	89.8(1)	C(7)-P(1)-Ru(1)	109.5(1)
C(13)-P(1)-Ru(1)	120.1(1)	C(20)-P(1)-Ru(1)	126.7(1)
C(7)-P(1)-C(13)	100.8(1)	C(7)-P(1)-C(20)	106.6(1)
C(13)-P(1)-C(20)	89.3(1)	C(13)-Pd(1)-C(20)	76.8(1)
C(13)-Pd(1)-N(2)	174.8(1)	C(13)-Pd(1)-Cl(3)	93.1(1)
C(20)-Pd(1)-N(2)	98.9(1)	C(20)-Pd(1)-Cl(3)	169.7(1)
N(2)-Pd(1)-Cl(3)	91.1(1)	C(14)-C(13)-P(1)	124.9(3)
C(14)-C(13)-Pd(1)	101.5(2)	P(1)-C(13)-Pd(1)	91.5(1)
C(21)-C(20)-P(1)	129.2(2)	C(21)-C(20)-Pd(1)	134.8(2)
P(1)-C(20)-Pd(1)	95.2(1)	N(1)-C(14)-C(13)	122.3(3)
N(1)-C(14)-C(15)	119.8(3)	C(13)-C(14)-C(15)	117.8(3)
C(14)-N(1)-C(16)	141.0(2)		

5.2.4.3 2D ROESY Studies of Complexes ($R_P S_C S_C$)-**37** and ($S_P R_C S_C$)-**38**

The structures of ($R_P S_C S_C$)-**37** and ($S_P R_C S_C$)-**38** have been studied through the 2D rotating frame nuclear Overhauser enhancement (ROESY) ^1H NMR technique. Scheme 5-8 shows the numbering scheme of ($R_P S_C S_C$)-**37** and ($S_P R_C S_C$)-**38** used in the 2D ROESY NMR analysis. Selected ^{31}P and ^1H NMR data of ($R_P S_C S_C$)-**37** and ($S_P R_C S_C$)-**38** are given in Table 5-6. These NMR assignments are based on a series of ^1H , ^{31}P , $^1\text{H}\{^{31}\text{P}\}$, and 2D ROESY NMR studies. Figures 5-6 and 5-7 show the 2D ^1H - ^1H ROESY NMR spectra of ($R_P S_C S_C$)-**37** and ($S_P R_C S_C$)-**38**, respectively.

Scheme 5-8

Table 5-6. Selected ^{31}P and ^1H NMR Spectra Chemical Shift Values of ($R_{\text{P}}S_{\text{C}}S_{\text{C}}$)-37 and ($S_{\text{P}}R_{\text{C}}S_{\text{C}}$)-38 in CDCl_3 (coupling constants in Hz are given in parentheses)

	($R_{\text{P}}S_{\text{C}}S_{\text{C}}$)-37	($S_{\text{P}}R_{\text{C}}S_{\text{C}}$)-38
^{31}P	44.3 s. br.	43.9 s. br.
NCHMe	1.70 d, ($^3J_{\text{HH}} = 7.0$)	1.38 d, ($^3J_{\text{HH}} = 7.0$)
$\text{N}=\text{C}-\text{Me}$	2.32 s	2.24 s
$\text{C}=\text{C}-\text{Me}$	2.51 Overlapped with signal of NMe(ax)	2.45 s
NMe(ax)	2.51 Overlapped with signal of $\text{C}=\text{C}-\text{Me}$	2.35 s
NMe(eq)	2.57 s	2.64 s
PdCH	2.63 s	2.71 s
NCHMe	3.10 q ($^3J_{\text{HH}} = 7.0$)	4.25 q ($^3J_{\text{HH}} = 7.0$)
C_6H_6	5.18 s	5.13 s
o-PPh	7.81-7.82 m	7.79-7.87 m

Figure 5-6. Two-dimensional ^1H ROESY NMR spectrum of $(R_p\text{SCSC})$ -**37** in CDCl_3 . All off-diagonal peaks are of negative intensity. Selected NOE contacts: A, Me24-H23; B, H23-H22; C, H18-Me19; D, Me16-Me9; E, Me16-Me17(eq); F, H16-Me17(eq); G, H16-Me17(ax); H, Me19-H21; I, Me16-H16; J, H21-H22; K, Me9- C_6H_6 ; L, H16-H14; M, Me17(ax)-H14; N, Me9-H11; O, C_6H_6 -H2,6; P, H18-H2,6; Q, Me16-H2,6; R, H20-H21.

Figure 5-7. Two-dimensional ^1H ROESY NMR spectrum of $(S_pR_cS_c)\text{-38}$ in CDCl_3 . All off-diagonal peaks are of negative intensity. Selected NOE contacts: A, Me24-H23; B, H23-H22; C, Me16-Me17(ax); D, Me16-Me17(eq); E, H23-H21; F, Me17(ax)-Me17(eq); G, Me19-H18; H, Me19-H21; I, H21-H22; J, Me17(eq)-H16; K, Me16-H16; L, Me9- C_6H_6 ; M, Me9-H12; N, Me9-H11; O, Me17(ax)-H14; P, Me16-H14; Q, C_6H_6 -H2,6; R, H16-H2,6; S, H18-H2,6; T, Me17(eq)-H2,6; U, H21-H20.

Through a Dreiding model study, the proposed structure of complex $(S_pR_cS_c)\text{-38}$ is shown in Scheme 5-8. The differences between the two spectra of complexes

($R_P S_C S_C$)-**37** and ($S_P R_C S_C$)-**38** are significant. The 2D ROESY NMR spectrum of ($R_P S_C S_C$)-**37** clearly shows the interactions (F, G) between H16 and the two NMe(Me17) groups. However, Me16 only interacts with the equatorial NMe group [E, Me16-Me17(eq)], while the interaction of Me16-Me17(eq) has not been observed. These signals reflect that Me16 occupies the axial position in complex ($R_P S_C S_C$)-**37**, which is in accordance with the result of the X-ray analysis. Moreover, H16, rather than Me16, interacts with the neighboring aromatic proton, H14 (L), which also suggests that the involved equatorial and axial groups are H16 and Me16, respectively in complex ($R_P S_C S_C$)-**37**. In contrast, Me16 in complex ($S_P R_C S_C$)-**38** was equatorially disposed according to the results of similar NMR studies. The 2D ROESY NMR spectrum of ($S_P R_C S_C$)-**38** shows the interactions of Me16-Me17(ax) (C), Me16-Me17(eq) (D), and Me17(eq)-H16 (J), while there is no signal resulting from the interaction of Me17(ax)-H16. Additionally, Me16, rather than H16, is observed to interact with the aromatic proton, H14, producing signal P (Me16-H14), which also indicates that Me16 occupies the equatorial position in complex ($S_P R_C S_C$)-**38**.

The 2D ROESY studies also indicate that the interactions involving the coordinated benzene ligand, the PPh group, the NMe groups, and the axial group on C16 are similar in complexes ($R_P S_C S_C$)-**37** and ($S_P R_C S_C$)-**38**. *o*-PPh(H2,6) is found to interact with the axial group on C16 to generate a clear signal [Me16-H2,6, Q in the case ($R_P S_C S_C$)-**37** and H16-H2,6, R in the case of ($S_P R_C S_C$)-**38**]. Moreover, the interaction between *o*-PPh(H2,6) and the equatorial NMe group, Me17(eq), has also been recorded in the 2D ROESY NMR spectrum of complex ($S_P R_C S_C$)-**38**, although the corresponding signal (T) is very

weak. However, for complex ($R_P S_C S_C$)-**37**, the NOE signal resulting from the interaction of Me17(eq)-H2,6 has not been observed due to the relative long distance, which is attributed to the repulsion between Me9 and the axially disposed Me16. In contrast, the interactions between the coordinated benzene and the NMe groups (Me17) or the substituents on C16 (Me16 and H16) are not found in both complexes. These interactions involving the coordinated benzene, the PPh group, the NMe groups, H16, and Me16 indicate that the PPh group, rather than the coordinated benzene, is close to the NMe groups (Me17) and C16, which allows the assignments of the *R* and *S* absolute configurations at phosphorus in complexes ($R_P S_C S_C$)-**37** and ($S_P R_C S_C$)-**38**, respectively. It is noteworthy that the configurations at phosphorus in both complexes are retained after hydroamination. Additionally, H18, rather than Me19 or H20, interacts with *o*-PPh(H2,6) [P in the case of ($R_P S_C S_C$)-**37** and S in the case of ($S_P R_C S_C$)-**38**], which suggests that H18 is *syn* to the PPh group, allowing the assignments of the *S* and *R* absolute configurations at C18 in complexes ($R_P S_C S_C$)-**37** and ($S_P R_C S_C$)-**38**, respectively.

These signals in the 2D ROESY NMR spectra are consistent with the X-ray structure of complex ($R_P S_C S_C$)-**37** and the interactions expected from the structures of both complexes in Scheme 5-8, thus confirming their configurations in solution.

5.2.5 Hydroamination Reactions Involving *t*-Butylamine

Additions of bulky *t*-butylamine to the insertion products **23**, ($R_{Ru} R_P S_C$)-**22**, and ($R_{Ru} S_P S_C$)-**22** have been studied. Due to the steric bulk of *t*-butylamine, a higher reaction

temperature is necessary. The reaction was carried out in chloroform at 40 °C. After the reaction was completed, as indicated by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, the crude reaction mixture was then purified by silica gel column chromatography and subsequently precipitated by hexane to give the corresponding product.

When monitored by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, the reaction of complex **23** and *t*-butylamine was found to be complete in 1.5 days. In CDCl_3 the resulting reaction mixture exhibited a broad singlet at δ 40.7 in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. Silica gel column chromatography and the subsequent precipitation by hexane gave **39** as a yellow solid in 33% yield (Scheme 5-9). In CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **39** showed a broad singlet at δ 40.7.

Scheme 5-9

The reaction of complex ($R_{\text{Ru}}R_{\text{P}}S_{\text{C}}$)-**22** and *t*-butylamine gave the hydroamination product ($R_{\text{P}}S_{\text{C}}S_{\text{C}}$)-**40**. When monitored by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, the reaction of complex ($R_{\text{Ru}}R_{\text{P}}S_{\text{C}}$)-**22** and 2 equiv of. *t*-butylamine was found to be complete in 1 day. In CDCl_3 the resulting reaction mixture exhibited a broad singlet at δ 39.8 in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. Unfortunately, attempted purification through silica gel column

chromatography and recrystallization failed to isolate the pure product. The crude product was isolated by silica gel column chromatography and subsequently precipitated by hexane as a yellow-orange solid in 20% yield (Scheme 5-10). In CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of crude $(R_{\text{P}}S_{\text{C}}S_{\text{C}})$ -**40** showed a broad singlet at δ 39.8.

Scheme 5-10

The reaction of complex $(R_{\text{Ru}}S_{\text{P}}S_{\text{C}})$ -**22** and t -butylamine gave the hydroamination product $(S_{\text{P}}R_{\text{C}}S_{\text{C}})$ -**41** in similar yield. When monitored by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, the reaction of complex $(R_{\text{Ru}}S_{\text{P}}S_{\text{C}})$ -**22** and 2 equiv of t -butylamine was found to be complete in 1.5 days. In CDCl_3 the resulting reaction mixture exhibited a broad singlet at δ 40.0 in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. Silica gel column chromatography and the subsequent precipitation by hexane gave $(S_{\text{P}}R_{\text{C}}S_{\text{C}})$ -**41** as a yellow solid in 23% yield (Scheme 5-11). In CDCl_3 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $(S_{\text{P}}R_{\text{C}}S_{\text{C}})$ -**41** showed a broad singlet at δ 40.0.

Scheme 5-11

5.2.6 Hydroamination Reactions Involving N-methylaniline

The secondary amine, N-methylaniline, was also found to react with the insertion products **23**, (R_{Ru}R_PS_C)-**22**, or (R_{Ru}S_PS_C)-**22** to give the desired products. For the nonchiral reactant **23**, the reaction proceeded smoothly in dichloromethane at room temperature. However, for the chiral reactant (R_{Ru}S_PS_C)-**22**, a higher reaction temperature is necessary. Moreover, the desired product was not observed during the reaction involving the diastereomeric complex (R_{Ru}R_PS_C)-**22** under similar conditions.

Hydroamination of complex **23** was found to be complete in 3 days at room temperature in dichloromethane. After hydroamination, in CDCl₃ the ³¹P{¹H} NMR spectrum of the reaction mixture exhibited a sharp singlet at δ 40.8. The crude mixture was then purified by silica gel column chromatography and subsequently precipitated by hexane to give the product **42** as a yellow solid in 34% yield (Scheme 5-12). Recrystallization of **42** from dichloromethane and diethyl ether gave red needles. In CDCl₃ the ³¹P{¹H} NMR spectrum of **42** showed a sharp singlet at δ 40.8.

Scheme 5-12

The reaction of complex (*R*_{Ru}*S*_P*S*_C)-**22** and N-methylaniline gave the hydroamination product (*S*_P*R*_C*S*_C)-**43** in similar yield. When monitored by the ³¹P{¹H} NMR spectroscopy, the reaction of complex (*R*_{Ru}*S*_P*S*_C)-**22** and N-methylaniline was found to be complete in 1.5 days at 40 °C in chloroform. In CDCl₃ the resulting reaction mixture exhibited a sharp singlet at δ 41.8 in the ³¹P{¹H} NMR spectrum. Silica gel column chromatography and the subsequent precipitation by hexane gave (*S*_P*R*_C*S*_C)-**43** as a yellow solid in 26% yield. In CDCl₃ the ³¹P{¹H} NMR spectrum of (*S*_P*R*_C*S*_C)-**43** showed a broad singlet at δ 41.8 (Scheme 5-13).

Scheme 5-13

5.2.6.1 X-ray Structural Analysis of Complex **42**

The single crystal X-ray structure of complex **42** is shown in Figure 5-8. A pair of enantiomers exists with a ratio of 1:1 in each crystal unit cell. The geometry at ruthenium center exhibits the expected and usual "three-legged piano-stool" disposition. The η^6 -coordinated arene is in a "stool" position, while the "legs" comprise P and Cl atoms. The angles at the Ru center are in the range of 85.1(1)-88.4(1)°. There is a 4-membered ring adopting a slightly distorted planar geometry, which is composed of Pd(1), P(1), C(13), and C(25), in this molecule. The four angles at the vertexes of this 4-membered ring, C(13)-Pd(1)-C(25) [77.3(2)°], P(1)-C(13)-Pd(1) [93.0(3)°], C(13)-P(1)-C(25) [90.7(3)°], and P(1)-C(25)-Pd(1) [88.6(2)°], are distinctly smaller than those observed in normal geometry, which is attributed to the ring constraints. Additionally, the bond length of C(26)-N(2) is 1.322(8) Å, which indicates the generation of a double bond between these two atoms. Therefore an imine, instead of an enamine, has been formed in the product. Although the imine moiety was formed after hydroamination, the methyl group, C28, and the phenyl group, C29-C34, still connect to nitrogen, which is responsible for the positive charge on the nitrogen atom. It is noteworthy that the C(25)-C(26) bond length is only 1.426(8) Å, which is shorter than the normal single carbon-carbon bond length. The absolute configuration of the structure shown in Figure 5-8 is designated as $S_P R_C$, while its enantiomer adopts the $R_P S_C$ absolute configuration. Selected bond distances and angles for complex **42** are given in Table 5-7.

Figure 5-8. Molecular structure of complex **42**.

Table 5-7. Selected Bond Lengths (Å) and Angles (deg) of **42**

Ru(1)-P(1)	2.352(2)	Ru(1)-Cl(2)	2.422(2)
Ru(1)-Cl(3)	2.405(2)	P(1)-C(7)	1.838(6)
P(1)-C(13)	1.796(6)	P(1)-C(25)	1.825(6)
Pd(1)-C(13)	2.005(6)	Pd(1)-C(25)	2.118(6)
Pd(1)-N(1)	2.148(5)	Pd(1)-Cl(1)	2.419(2)
C(13)-C(14)	1.356(9)	C(25)-C(26)	1.426(8)
C(26)-N(2)	1.322(8)	C(28)-N(2)	1.480(8)
P(1)-Ru(1)-Cl(2)	85.1(1)	P(1)-Ru(1)-Cl(3)	88.1(1)
Cl(2)-Ru(1)-Cl(3)	88.4(1)	C(7)-P(1)-Ru(1)	108.9(2)

C(13)-P(1)-Ru(1)	131.4(2)	C(25)-P(1)-Ru(1)	120.1(2)
C(7)-P(1)-C(13)	101.8(3)	C(7)-P(1)-C(25)	98.2(3)
C(13)-P(1)-C(25)	90.7(3)	C(13)-Pd(1)-C(25)	77.3(2)
C(13)-Pd(1)-N(1)	97.5(2)	C(13)-Pd(1)-Cl(1)	170.1(2)
C(25)-Pd(1)-N(1)	167.7(2)	C(25)-Pd(1)-Cl(1)	92.9(2)
N(1)-Pd(1)-Cl(1)	91.9(2)	C(14)-C(13)-P(1)	131.6(5)
C(14)-C(13)-Pd(1)	134.8(5)	P(1)-C(13)-Pd(1)	93.0(3)
C(26)-C(25)-P(1)	126.7(5)	C(26)-C(25)-Pd(1)	100.6(4)
P(1)-C(25)-Pd(1)	88.6(2)	N(2)-C(26)-C(25)	119.8(6)
N(2)-C(26)-C(27)	116.7(6)	C(25)-C(26)-C(27)	123.5(5)
C(26)-N(2)-C(28)	122.0(5)	C(26)-N(2)-C(29)	122.5(5)
C(28)-N(2)-C(29)	115.0(5)		

5.2.7 H-D Exchange Studies on the Products Generated by Reactions Involving Primary Amines

It is noteworthy that the hydroamination products generated by the reactions involving primary amines contain a protonized N-substituted imine moiety. In CDCl₃ this proton shows a typical singlet at very low field ranging from δ 8.5-10.5 in the ¹H NMR spectra, which were proved by H-D exchange studies. Upon mixing a drop of D₂O with the involving solution in CDCl₃, the N-H signal disappeared within several minutes due to the exchange process between H⁺ on nitrogen and D⁺ in D₂O.

The N-substituted imine moiety is observed to be protonized, which balances the negative charge at palladium. Furthermore, due to the positive charge that is located at the protonized N-substituted imine moiety in hydroamination products, the nitrogen of this imino group does not coordinate to ruthenium. There are two possible reasons for the formation of the protonized N-substituted imino group instead of the positive N-coordinated ruthenium center, which has been observed in the hydration products in Chapter 4. One is the hindrance resulting from the substituent on nitrogen, which keeps the imino group from approaching the metal. The other reason is related to the electronic property of the imine moiety. Since the C=NR group is more basic than the C=O unit, the nitrogen atom is more facile to be protonized than the oxygen atom.

5.2.8 Absolute Configurations of Hydroamination Products

After hydroamination, the chirality at ruthenium was lost as the Pd-Cl bond was cleaved. However, this process generated a stereogenic center at the carbon at the α -position from phosphorus and palladium. Moreover, when the chiral substrates, ($R_{Ru}R_P S_C$)-**22** and ($R_{Ru} S_P S_C$)-**22**, were used, the configuration at phosphorus remained unchanged in the product as well as that of the carbon neighboring the NMe groups.

In all hydroamination products, it is interesting that the phenyl group on phosphorus always occupies the *syn* position to the hydrogen on the chiral carbon and is distal to the imine moiety, as illustrated in Scheme 5-14a. It is proposed that the formation of this absolute configuration at the stereogenic carbon center is affected by the chiral center at

the phosphorus atom. As shown in Scheme 5-14b, during the tautomerization process (See Section 5.2.11), the electrophilic attack of a proton on the alkene moiety from the bottom side, leading to the generation of the structure in Scheme 5-14a, is favored, which is attributed to the less bulky phenyl group. Therefore, hydroamination of the nonchiral substrate **23** only gave racemates adopting the $R_P S_C$ and $S_P R_C$ absolute configurations, and those reactions involving the chiral substrate, $(R_{Ru} R_P S_C)$ -**22** or $(R_{Ru} S_P S_C)$ -**22**, generated an optically pure product stereoselectively, in which the hydrogen on the stereogenic carbon center occupied the *syn* position to the phenyl group on the chiral phosphorus atom.

Scheme 5-14

5.2.9 Structural Features of Hydroamination Products

The hydroamination products have two interesting structural features that are similar to those of the hydration products. Firstly, a Pd-C-P-C 4-membered ring, which deviates slightly from planarity, was formed in the products. The ring constraints are responsible for the smaller than the normal angles at the vertices. Secondly, the hydroamination products are bimetallic zwitterions bearing a positive charge at the imine moiety and a negative charge at palladium.

5.2.10 Comparison of Reactivities

For complexes **23** and $(R_{Ru}S_P S_C)$ -**22**, the reactivity of hydroamination is much higher than that of hydration, which is indicated by the much shorter reaction time and the higher yields obtained. Furthermore, comparing the two diastereomeric chiral complexes $(R_{Ru}R_P S_C)$ -**22** and $(R_{Ru}S_P S_C)$ -**22**, the former is less reactive toward hydroamination than the latter. Complex $(R_{Ru}S_P S_C)$ -**22** was observed to react with *n*-, *t*-butylamine, aniline, and N-methylaniline smoothly to give the hydroamination products. In contrast, complex $(R_{Ru}R_P S_C)$ -**22** could only undergo the hydroamination reactions involving *n*- and *t*-butylamine, while the reactions involving aniline and N-methylaniline could not proceed under similar conditions.

5.2.11 Mechanistic Considerations

The mechanism of hydroamination is suggested to be similar to that of hydration. Aided by palladium, the nucleophilic attack of amine on the alkynyl group generates the enamine intermediate **45**, which subsequently undergoes the tautomerization to give the hydroamination product (Scheme 5-15). It is noteworthy that these hydroamination processes involved in this Chapter exhibited good regioselectivities since the newly formed imino group was always found to bond to the carbon β to the phosphorus atom in all products.

Scheme 5-15 (the square indicates the vacant coordination site)

5.3 Conclusions

The hydroamination reactions of the insertion products ($R_{Ru}R_PSC$)-**22** ($R_{Ru}S_PSC$)-**22**, and **23** have been studied. These reactions converted the alkynyl group in the involved complexes into an imino group under mild condition, thus yielding bifunctionalized phosphine complexes. A variety of amines, including the bulky and secondary amines, exhibited high reactivities toward these complexes. It is noteworthy that for complexes ($R_{Ru}R_PSC$)-**22** and ($R_{Ru}S_PSC$)-**22**, which contains a chiral center at phosphorus, the absolute configuration at phosphorus remained unchanged after the hydroamination process. Furthermore, the newly generated imino group is observed to bond to the carbon β to the phosphorus atom regioselectively. The X-ray crystallographic analysis confirmed that an unusual 4-membered ring, which adopted a slightly distorted planar geometry, was formed during the hydroamination reactions. Additionally, the product molecules are zwitterionic bimetallic complexes, which contain a positive charge at the protonized N-substituted imine moiety and a negative charge at palladium.

5.4 Experimental

Synthesis of Complex **32**

Complex **23** (0.210 g, 0.295 mmol) was stirred with aniline (0.033 g, 0.354 mmol) in dichloromethane (25 mL) at room temperature for 1.5 days. The resulting solution was then concentrated and purified by silica gel column chromatography (acetone-dichloromethane 1:10). The subsequent precipitation by diethyl ether gave **32** as

a yellow solid. Yield: 0.135 g (57%). Complex **32** was recrystallized from dichloromethane and diethyl ether as red prisms, which were suitable for X-ray analysis. Mp: 186-187 °C dec. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 41.0 (s, br.). ^1H NMR (CDCl_3 , δ): 2.24 (s, 3H, $\text{N}=\text{C}-\text{Me}$); 2.44 (m, 6H, $\text{C}=\text{C}-\text{Me}$ and NMe); 2.61 (s, 3H, NMe); 3.02 (d, $^2J_{\text{HH}} = 11.0$ Hz, 1H, PdNCHH); 3.22 (d, $^2J_{\text{PH}} = 5.3$ Hz, 1H, PdCH); 3.96 (d, $^2J_{\text{HH}} = 11.0$ Hz, 1H, PdNCHH); 5.22 (s, 6H, C_6H_6); 7.14-7.29 (9H), 7.57-7.61 (1H), 7.67-7.72 (2H), 7.87-7.93 (2H) (m, *aromatics*); 10.38 (s, 1H, NH). Anal. Calcd for $\text{C}_{33}\text{H}_{36}\text{Cl}_3\text{N}_2\text{PPdRu}$: C, 49.2; H, 4.5; N, 3.5. Found: C, 49.2; H, 4.7; N, 3.5.

Synthesis of Complex ($S_{\text{P}}R_{\text{C}}S_{\text{C}}$)-33

Complex ($R_{\text{Ru}}S_{\text{P}}S_{\text{C}}$)-**22** (0.039 g, 0.054 mmol) was stirred with aniline (0.007 g, 0.075 mmol) in dichloromethane (5 mL) at room temperature for 1.5 days. The resulting solution was then concentrated and purified by silica gel column chromatography (acetone-dichloromethane 1:10). The subsequent precipitation by hexane gave ($S_{\text{P}}R_{\text{C}}S_{\text{C}}$)-**33** as a yellow solid. Yield: 0.029 g (64%). Mp: 185-186 °C dec. $[\alpha]_{\text{D}} +506.0^\circ$ (c 0.5, CHCl_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 41.3 (s, br.). ^1H NMR (CDCl_3 , δ): 1.40 (d, $^3J_{\text{HH}} = 7.0$ Hz, 3H, NCHMe); 2.22 (s, 3H, $\text{N}=\text{C}-\text{Me}$); 2.43 (m, 6H, $\text{C}=\text{C}-\text{Me}$ and NMe); 2.66 (s, 3H, NMe); 3.22 (d, $^2J_{\text{PH}} = 5.4$ Hz, 1H, PdCH); 4.26 (q, $^3J_{\text{HH}} = 7.0$ Hz, 1H, NCHMe); 5.22 (s, 6H, C_6H_6); 7.13-7.31 (9H), 7.57-7.62 (1H), 7.67-7.73 (2H), 7.88-7.94 (2H) (m, *aromatics*); 10.37 (s, 1H, NH). Anal. Calcd for $\text{C}_{34}\text{H}_{38}\text{Cl}_3\text{N}_2\text{PPdRu}$: C, 49.8; H, 4.7; N, 3.4. Found: C, 49.8; H, 4.8; N, 3.5.

Synthesis of Complex **34**

Complex **23** (0.040 g, 0.056 mmol) was stirred with benzylamine (0.006 g, 0.056 mmol) in dichloromethane (5 mL) at room temperature for 2 days. The resulting solution was then concentrated and purified by silica gel column chromatography (acetone-dichloromethane 1:10). The subsequent precipitation by diethyl ether gave **34** as a yellow solid. Yield: 0.016 g (36%). Complex **34** was recrystallized from dichloromethane and diethyl ether as red prisms, which were suitable for X-ray analysis. Mp: 183-185 °C dec. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 42.2 (s, br.). ^1H NMR (CDCl_3 , δ): 2.21 (s, 3H, $\text{N}=\text{C}-\text{Me}$); 2.39 (s, 3H, NMe); 2.45 (s, 3H, $\text{C}=\text{C}-\text{Me}$); 2.61 (s, 3H, NMe); 2.94 (d, $^2J_{\text{PH}} = 4.6$ Hz, 1H, PdCH); 3.06 (1H), 3.98 (1H) (d, $^2J_{\text{HH}} = 10.9$ Hz, PdNCHH); 4.33-4.47 (m, 2H, $\text{CH}_2-\text{N}=\text{C}$); 5.20 (s, 6H, C_6H_6); 6.86-6.91 (2H); 7.05-7.27 (7H), 7.55-7.60 (1H), 7.65-7.70 (2H), 7.83-7.89 (2H) (m, *aromatics*); 9.39 (s, br. 1H, NH). Anal. Calcd for $\text{C}_{34}\text{H}_{38}\text{Cl}_3\text{N}_2\text{PPdRu}$: C, 49.8; H, 4.7; N, 3.4. Found: C, 49.7; H, 4.8; N, 3.4.

Synthesis of Complex **35**

Complex **23** (0.041 g, 0.057 mmol) was stirred with 2-phenylethylamine (0.008 g, 0.066 mmol) in dichloromethane (5 mL) at room temperature for 2 days. The resulting solution was then concentrated and purified by silica gel column chromatography (acetone-dichloromethane 1:10). The subsequent precipitation by hexane gave **35** as a yellow solid. Yield: 0.017 g (36%). Mp: 177-179 °C dec. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 42.6 (s, br.). ^1H NMR (CDCl_3 , δ): 2.13 (s, 3H, $\text{N}=\text{C}-\text{Me}$); 2.40 (s, 3H, NMe); 2.49 (d, $^4J_{\text{PH}} = 1.7$ Hz, 3H, $\text{C}=\text{C}-\text{Me}$); 2.58 (s, 3H, NMe); 2.73-3.04 (m, 3H, $\text{Ph CH}_2\text{CH}_2$); 2.80 (d, $^2J_{\text{PH}} = 3.1$ Hz, 1H, PdCH); 3.02 (d, $^2J_{\text{HH}} = 10.9$ Hz, 1H, PdNCHH); 3.29-3.41 (m, 3H, PhCH_2CH_2); 3.95 (d, $^2J_{\text{HH}} = 10.9$ Hz, 1H, PdNCHH); 4.33-4.47 (m, 2H, $\text{CH}_2-\text{N}=\text{C}$); 5.20

(s, 6H, C_6H_6); 7.10-7.26 (7H); 7.30-7.36 (1H), 7.41-7.43 (1H), 7.54-7.59 (1H), 7.64-7.68 (2H), 7.81-7.88 (2H) (m, *aromatics*); 9.04 (s, br. 1H, NH). Anal. Calcd for $C_{35}H_{40}Cl_3N_2PPdRu$: C, 50.4; H, 4.8; N, 3.4. Found: C, 50.4; H, 5.1; N, 3.6.

Synthesis of Complex **36**

Complex **23** (0.911 g, 1.280 mmol) was stirred with *n*-butylamine (0.275 g, 3.760 mmol) in dichloromethane (90 mL) at room temperature for 1 day. The resulting solution was then concentrated and purified by silica gel column chromatography (acetone-dichloromethane 1:10). The subsequent precipitation by hexane gave **36** as an orange solid. Yield: 0.286 g (28%). Complex **36** was recrystallized from dichloromethane and diethyl ether as red prisms, which were suitable for X-ray analysis. Mp: 194-195 °C dec. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 43.1 (s, br.). 1H NMR ($CDCl_3$, δ): 0.72 [t, $^3J_{HH} = 7.3$ Hz, 3H, $N(CH_2)_3-Me$]; 1.18-1.28 [m, 2H, $N(CH_2)_2-CH_2Me$]; 1.47-1.63 (m, 2H, $NCH_2-CH_2-CH_2Me$); 2.25 (s, 3H, $N=C-Me$); 2.35 (s, 3H, $C=C-Me$); 2.46 (3H), 2.58 (3H) (s, *NMe*); 2.72 (d, $^2J_{PH} = 2.6$ Hz, 1H, $PdCH$); 3.00 (d, $^2J_{HH} = 10.9$ Hz, 1H, $PdNCHH$); 3.11-3.16 [m, 2H, $NCH_2-(CH_2)_2Me$]; 3.93 (d, $^2J_{HH} = 10.9$ Hz, 1H, $PdNCHH$); 5.17 (s, 6H, C_6H_6); 7.12-7.14 (1H), 7.19-7.24 (1H), 7.31-7.41 (2H), 7.53-7.67 (3H), 7.81-7.83 (2H) (m, *aromatics*); 8.87 (s, 1H, NH). Anal. Calcd for $C_{31}H_{40}Cl_3N_2PPdRu \cdot H_2O$: C, 46.3; H, 5.3; N, 3.5. Found: C, 46.2; H, 5.1; N, 3.6.

Synthesis of Complex ($R_P S_C S_C$)-**37**

Complex ($R_{Ru} R_P S_C$)-**22** (0.211 g, 0.290 mmol) was stirred with *n*-butylamine (0.042 g, 0.580 mmol) in dichloromethane (20 mL) at room temperature for 1 day. The resulting

solution was then concentrated and purified by silica gel column chromatography (acetone-dichloromethane 1:8). The subsequent precipitation by hexane gave ($R_P S_C S_C$)-**37** as a yellow-orange solid. Yield: 0.042 g (25%). Complex ($R_P S_C S_C$)-**37** was recrystallized from dichloromethane and diethyl ether as red needles, which were suitable for X-ray analysis. Mp: 219-221 °C dec. $[\alpha]_D = 172.7^\circ$ (c 0.5, $CHCl_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 44.3 (s, br.). 1H NMR ($CDCl_3$, δ): 0.61 [t, $^3J_{HH} = 7.3$ Hz, 3H, $N(CH_2)_3Me$]; 1.11-1.25 [m, 2H, $N(CH_2)_2CH_2Me$]; 1.39-1.52 (m, 2H, $NCH_2CH_2CH_2Me$); 1.70 (d, $^3J_{HH} = 7.0$ Hz, 3H, $NCHMe$); 2.32 (s, 3H, $N=C-Me$); 2.51 (s, 6H, NMe and $C=C-Me$); 2.57 (s, 3H, NMe); 2.63 (s, 1H, $PdCH$); 3.10 (q, $^3J_{HH} = 7.0$ Hz, $NCHMe$); 3.15-3.23 [m, 2H, $NCH_2-(CH_2)_2Me$]; 5.18 (s, 6H, C_6H_6); 6.99-7.01 (1H), 7.13-7.16 (1H), 7.27-7.29 (1H), 7.37-7.39 (1H), 7.53-7.58 (1H), 7.63-7.66 (2H), 7.81-7.82 (2H), (m, *aromatics*); 8.76 (s, 1H, NH). Anal. Calcd for $C_{32}H_{42}Cl_3N_2PPdRu \cdot H_2O$: C, 47.0; H, 5.4; N, 3.4. Found: C, 46.7; H, 5.4; N, 3.5.

Synthesis of Complex ($S_P R_C S_C$)-**38**

Complex ($R_{Ru} S_P S_C$)-**22** (0.203 g, 0.280 mmol) was stirred with *n*-butylamine (0.041 g, 0.560 mmol) in dichloromethane (20 mL) at room temperature for 1 day. The resulting solution was then concentrated and purified by silica gel column chromatography (acetone-dichloromethane 1:10). The subsequent precipitation by hexane gave ($S_P R_C S_C$)-**38** as an orange solid. Yield: 0.041 g (18%). Mp: 210-212 °C dec. $[\alpha]_D +377.4^\circ$ (c 0.5, $CHCl_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 43.9 (s, br.). 1H NMR ($CDCl_3$, δ): 0.8 [t, $^3J_{HH} = 7.3$ Hz, 3H, $N(CH_2)_3Me$]; 1.20-1.26 [m, 2H, $N(CH_2)_2CH_2Me$]; 1.38 (d, $^3J_{HH} = 7.0$ Hz, 3H, $NCHMe$); 1.47-1.59 (m, 2H, $NCH_2CH_2CH_2Me$); 2.24 (s, 3H, $N=C-Me$); 2.35 (s,

3H, *NMe*); 2.45 (s, 3H, C=C-*Me*); 2.64 (s, 3H, *NMe*); 2.71 (s, 1H, PdCH); 3.10-3.15 [m, 2H, NCH₂-(CH₂)₂Me]; 4.25 (q, ³J_{HH} = 7.0 Hz, 1H, NCHMe); 5.13 (s, 6H, C₆H₆); 7.22-7.25(1H), 7.27-7.29 (2H), 7.33-7.35 (1H), 7.55-7.58 (1H), 7.65-7.67 (2H), 7.79-7.87(2H), (m, 3H, *aromatics*); 8.85 (s, 1H, NH). Anal. Calcd for C₃₂H₄₂Cl₃N₂PPdRu·CH₂Cl₂: C, 44.8; H, 5.0; N, 3.2. Found: C, 44.8; H, 4.8; N, 3.4.

Synthesis of Complex **39**

Complex **23** (0.212 g, 0.300 mmol) was stirred with *t*-butylamine (0.028 g, 0.380 mmol) in chloroform (20 mL) at 40 °C for 1.5 days. The resulting solution was then concentrated and purified by silica gel column chromatography (acetone-dichloromethane 1:6). The subsequent precipitation by hexane gave **39** as a yellow solid. Yield: 0.075 g (33%). Mp: 219-222 °C dec. ³¹P{¹H} NMR (CDCl₃, δ): 40.7 (s, br.). ¹H NMR (CDCl₃, δ): 1.35 (s, 9H, NCMe₃); 2.36 (s, 3H, N=C-*Me*); 2.42 (s, 3H, *NMe*); 2.51 (d, ⁴J_{PH} = 1.3 Hz, 3H, C=C-*Me*); 2.55 (s, 3H, *NMe*); 2.71 (d, ²J_{PH} = 2.5 Hz, 1H, PdCH); 3.01 (d, ²J_{HH} = 11.0 Hz, 1H, PdNCHH); 3.94 (d, ²J_{HH} = 11.0 Hz, 1H, PdNCHH); 5.16 (s, 6H, C₆H₆); 7.14-7.24 (2H), 7.35-7.46 (2H), 7.52-7.67 (3H), 7.82-7.88 (2H) (m, *aromatics*); 8.40 (s, 1H, NH). Anal. Calcd for C₃₁H₄₀Cl₃N₂PPdRu·H₂O: C, 46.3; H, 5.3; N, 3.5. Found: C, 46.6; H, 5.2; N, 3.7.

Synthesis of Complex (R_PS_CS_C)-**40**

Complex (R_{Ru}R_PS_C)-**22** (0.200 g, 0.270 mmol) was stirred with *t*-butylamine (0.044 g, 0.600 mmol) in chloroform (20 mL) at 40 °C for 1 day. The resulting solution was then concentrated and isolated by silica gel column chromatography

(acetone-dichloromethane 1:10). The subsequent precipitation by hexane gave crude (*R_PS_CS_C*)-**40** as a yellow-orange solid. Yield: 0.043 g (20%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 39.8 (s, br.).

Synthesis of Complex (*S_PR_CS_C*)-**41**

Complex (*R_{Ru}S_PS_C*)-**22** (0.208 g, 0.290 mmol) was stirred with *t*-butylamine (0.044 g, 0.600 mmol) in dichloromethane (20 mL) at 40 °C for 1.5 days. The resulting solution was then concentrated and purified by silica gel column chromatography (acetone-dichloromethane 1:6). The subsequent precipitation by hexane gave (*S_PR_CS_C*)-**41** as a yellow solid. Yield: 0.053 g (23%). Mp: 213-215 °C dec. $[\alpha]_{\text{D}} +386.0^\circ$ (*c* 0.9, CHCl_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 40.0 (s, br.). ^1H NMR (CDCl_3 , δ): 1.34 (s, 9H, NMe_3); 1.38 (d, $^3J_{\text{HH}} = 7.0$ Hz, 3H, NCHMe); 2.37 (s, 3H, $\text{N}=\text{C-Me}$); 2.42 (s, 3H, NMe); 2.49 (d, $^4J_{\text{PH}} = 2.1$ Hz, 3H, $\text{C}=\text{C-Me}$); 2.61 (s, 3H, NMe); 2.66 (d, $^2J_{\text{PH}} = 3.1$ Hz, PdCH); 4.26 (q, $^3J_{\text{HH}} = 7.0$ Hz, 1H, NCHMe); 5.16 (s, 6H, C_6H_6); 7.29-7.41 (4H), 7.52-7.57 (1H), 7.63-7.67 (2H), 7.82-7.87 (2H), (m, *aromatics*); 8.38 (s, 1H, NH). Anal. Calcd for $\text{C}_{32}\text{H}_{42}\text{Cl}_3\text{N}_2\text{PPdRu}\cdot 0.5\text{CH}_2\text{Cl}_2$: C, 46.4; H, 5.2; N, 3.3. Found: C, 46.8; H, 4.8; N, 3.3.

Synthesis of Complex **42**

Complex **23** (0.770 g, 1.080 mmol) was stirred with *N*-methylaniline (0.129 g, 1.200 mmol) in dichloromethane (80 mL) at room temperature for 3 days. The resulting solution was then concentrated and purified by silica gel column chromatography (acetone-dichloromethane 1:10). The subsequent precipitation by hexane gave **42** as a yellow solid. Yield: 0.305 g (34%). Complex **42** was recrystallized from dichloromethane

and diethyl ether as red needles, which were suitable for X-ray analysis. Mp: 220-222 °C dec. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 40.8 (s). ^1H NMR (CDCl_3 , δ): 2.29 (s, 3H, N=C-Me); 2.35 (s, 3H, NMe); 2.55 (d, $^4J_{\text{PH}} = 1.9$ Hz, 3H, C=C-Me); 2.60 (s, 3H, NMe); 3.04 (d, $^2J_{\text{HH}} = 10.9$ Hz, 1H, NCHH); 3.08 (s, 1H, PdCH); 3.62 (s, 3H, C=N-Me); 4.00 (d, $^2J_{\text{HH}} = 10.9$ Hz, 1H, NCHH); 5.17 (s, 6H, C_6H_6); 7.12-7.24 (2H), 7.28-7.36 (6H), 7.42-7.46 (1H), 7.54-7.59 (1H), 7.65-7.70 (2H), 7.90-7.95 (2H), (m, aromatics). Anal. Calcd for $\text{C}_{34}\text{H}_{38}\text{Cl}_3\text{N}_2\text{PPdRu}\cdot 0.5\text{Et}_2\text{O}$: C, 50.5; H, 5.1; N, 3.3. Found: C, 50.7; H, 5.1; N, 3.0.

Synthesis of Complex ($S_{\text{P}}R_{\text{C}}S_{\text{C}}$)-43

Complex ($R_{\text{Ru}}S_{\text{P}}S_{\text{C}}$)-22 (0.206 g, 0.280 mmol) was stirred with N-methylaniline (0.035 g, 0.320 mmol) in chloroform (20 mL) at 40 °C for 1.5 days. The resulting solution was then concentrated and purified by silica gel column chromatography (acetone-dichloromethane 1:8). The subsequent precipitation by hexane gave ($S_{\text{P}}R_{\text{C}}S_{\text{C}}$)-43 as a yellow solid. Yield: 0.062 g (26%). Mp: 204-205 °C dec. $[\alpha]_{\text{D}} +44.3^\circ$ (c 0.7, CHCl_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 41.8 (s). ^1H NMR (CDCl_3 , δ): 1.41 (d, 3H, $^3J_{\text{HH}} = 7.0$ Hz, NCHMe); 2.25 (s, 3H, N=C-Me); 2.34 (s, 3H, NMe); 2.53 (d, 3H, $^4J_{\text{PH}} = 1.9$ Hz, C=CMe); 2.66 (s, 3H, NMe); 3.04 (s, 1H, PdCH); 3.60 (s, 3H, C=N-Me); 4.34 (q, 1H, $^3J_{\text{HH}} = 7.0$ Hz, NCHMe); 5.17 (s, 6H, C_6H_6); 7.21-7.24 (2H), 7.28-7.39 (7H), 7.56-7.70 (3H), 7.91-7.94 (2H), (m, aromatics). Anal. Calcd for $\text{C}_{35}\text{H}_{40}\text{Cl}_3\text{N}_2\text{PPdRu}\cdot 0.5\text{CH}_2\text{Cl}_2$: C, 48.7; H, 4.7; N, 3.2. Found: C, 48.8; H, 4.9; N, 2.9.

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Publications

Stepwise Functionalization of Two Alkyne Moieties in a Dialkynylphosphine Complex Leading to the Formation of a Bifunctionalized Phosphine Complex Bearing a Stereogenic Center at Phosphorus; Luo, D.; Li, Y.; Tan, K. W.; Leung, P. H. *Organometallics* **2009**, 28, 6266.

Syntheses of Bimetallic Zwitterionic Complexes Containing Stereogenic Bifunctionalized Phosphine through Stepwise Insertion and Hydration Reactions; Luo, D.; Li, Y.; Pullarkat, S. A.; Cockle, K. E.; Leung, P. H. *Organometallics* **2010**, 29, 893.

Asymmetric synthesis of dimethyl-1,2-bis-(diphenylphosphino)-1,2-ethanedicarboxylate by means of a chiral palladium template promoted hydrophosphination reaction; Tang, L.; Zhang, Y.; Luo, D.; Li, Y.; Mok, K. F.; Yeo, W. C.; Leung, P. H. *Tetrahedron Lett.* **2007**, 48, 33.

Appendices

X-ray Crystallographic Data

The X-ray structural analyses were kindly performed by Dr. Li Yongxin of 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.

Table A-1.1 Crystal Data and Structure Refinement for 3.

Empirical formula	C ₁₉ H ₁₉ Cl ₄ P Ru	
Formula weight	521.18	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 21.7708(6) Å	α = 90°.
	b = 7.5276(2) Å	β = 92.572(2)°.
	c = 25.4914(7) Å	γ = 90°.
Volume	4173.4(2) Å ³	
Z	8	
Density (calculated)	1.659 Mg/m ³	
Absorption coefficient	1.340 mm ⁻¹	
F(000)	2080	
Crystal size	0.34 x 0.30 x 0.18 mm ³	
Theta range for data collection	1.60 to 30.00°.	
Index ranges	-30 ≤ h ≤ 30, -9 ≤ k ≤ 10, -35 ≤ l ≤ 35	
Reflections collected	29188	
Independent reflections	6088 [R(int) = 0.0263]	
Completeness to theta = 30.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7944 and 0.6586	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6088 / 0 / 228	
Goodness-of-fit on F ²	1.216	
Final R indices [I > 2σ(I)]	R1 = 0.0259, wR2 = 0.0742	
R indices (all data)	R1 = 0.0331, wR2 = 0.0907	
Largest diff. peak and hole	0.756 and -0.799 e.Å ⁻³	

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad wR2 = \sqrt{\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}}, \quad w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP.$$

Table A-1.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 3. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	3341(1)	3281(1)	863(1)	17(1)
C(1)	3982(2)	2841(4)	257(2)	74(2)
C(2)	3413(2)	2125(4)	57(1)	53(1)
C(3)	3114(1)	905(4)	353(1)	40(1)
C(4)	3361(2)	385(4)	840(1)	48(1)
C(5)	3919(2)	973(5)	1021(1)	65(1)
C(6)	4237(1)	2210(7)	738(2)	80(2)
C(7)	3921(1)	3463(3)	2117(1)	28(1)
C(8)	4013(1)	2438(4)	2465(1)	40(1)
C(9)	4123(2)	1178(6)	2901(2)	74(1)
C(10)	3329(1)	6567(3)	1843(1)	24(1)
C(11)	3034(1)	7741(3)	2023(1)	26(1)
C(12)	2664(1)	9158(4)	2237(1)	38(1)
C(13)	4493(1)	5874(3)	1448(1)	22(1)
C(14)	5013(1)	5620(4)	1777(1)	37(1)
C(15)	5568(1)	6419(4)	1664(1)	44(1)
C(16)	5603(1)	7470(4)	1226(1)	36(1)
C(17)	5097(1)	7709(3)	892(1)	33(1)
C(18)	4541(1)	6906(3)	1000(1)	27(1)
C(19)	1552(1)	7060(3)	659(1)	30(1)
Cl(1)	2391(1)	3214(1)	1314(1)	25(1)
Cl(2)	3024(1)	6115(1)	522(1)	22(1)
Cl(3)	762(1)	6905(1)	476(1)	56(1)
Cl(4)	1721(1)	9032(1)	1007(1)	48(1)
P(1)	3753(1)	4848(1)	1574(1)	19(1)

Table A-2.1 Crystal Data and Structure Refinement for 5.

Empirical formula	C ₂₁ H ₁₉ Cl ₂ P Ru	
Formula weight	474.30	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 8.4075(4) Å	α = 90°.
	b = 13.5456(4) Å	β = 98.126(2)°.
	c = 17.3316(7) Å	γ = 90°.
Volume	1953.99(13) Å ³	
Z	4	
Density (calculated)	1.612 Mg/m ³	
Absorption coefficient	1.159 mm ⁻¹	
F(000)	952	
Crystal size	0.30 x 0.26 x 0.04 mm ³	
Theta range for data collection	2.56 to 29.18°.	
Index ranges	-11 ≤ h ≤ 11, -18 ≤ k ≤ 18, -23 ≤ l ≤ 23	
Reflections collected	28335	
Independent reflections	5271 [R(int) = 0.0516]	
Completeness to theta = 29.18°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9551 and 0.7225	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5271 / 530 / 365	
Goodness-of-fit on F ²	1.143	
Final R indices [I > 2σ(I)]	R1 = 0.0543, wR2 = 0.1042	
R indices (all data)	R1 = 0.0884, wR2 = 0.1166	
Largest diff. peak and hole	0.649 and -0.624 e.Å ⁻³	

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad wR2 = \sqrt{\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}}, \quad w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP.$$

Table A-2.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 5. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(7)	5189(10)	1518(7)	3232(6)	43(3)
C(8)	4688(8)	2275(5)	3450(3)	48(2)
C(9)	4122(12)	3195(7)	3753(6)	60(3)
C(7A)	8040(30)	400(30)	3460(20)	43(10)
C(8A)	9420(20)	400(20)	3792(19)	108(10)
C(9A)	10900(30)	170(20)	4329(17)	104(11)
C(10)	8139(13)	524(11)	3302(8)	44(3)
C(11)	9151(7)	-190(5)	3101(4)	60(2)
C(12)	10738(8)	-187(6)	3423(6)	89(3)
C(13)	11324(9)	547(8)	3927(7)	95(3)
C(14)	10304(10)	1221(8)	4144(7)	131(5)
C(15)	8693(8)	1206(7)	3848(5)	89(3)
C(10A)	5220(30)	1460(17)	3291(12)	57(13)
C(11A)	6090(20)	2216(12)	3663(11)	63(5)
C(12A)	5310(30)	3027(14)	3910(14)	89(7)
C(13A)	3680(30)	3032(19)	3883(18)	68(9)
C(14A)	2810(20)	2266(14)	3526(12)	79(6)
C(15A)	3590(20)	1475(13)	3260(10)	62(5)
C(1)	7460(30)	1985(18)	1747(12)	70(5)
C(2)	5970(30)	2252(16)	1337(14)	78(5)
C(3)	5467(19)	1816(15)	604(11)	68(4)
C(4)	6350(20)	1092(12)	291(7)	60(4)
C(5)	7830(20)	822(11)	733(11)	61(4)
C(6)	8407(18)	1244(16)	1465(10)	66(4)
C(1A)	7020(40)	2150(20)	1717(12)	58(5)
C(2A)	5740(30)	2190(20)	1107(14)	52(4)
C(3A)	5780(30)	1580(20)	453(11)	62(5)
C(4A)	7040(40)	918(18)	401(14)	65(6)
C(5A)	8280(30)	878(18)	1034(18)	73(6)
C(6A)	8310(30)	1490(20)	1691(16)	72(6)
Ru(1)	6026(1)	663(1)	1512(1)	52(1)
C(16)	5216(5)	-576(3)	3302(2)	43(1)
C(17)	4258(6)	-1272(4)	2885(3)	56(1)

C(18)	3623(6)	-2045(4)	3266(3)	60(1)
C(19)	3950(6)	-2130(3)	4066(3)	55(1)
C(20)	4899(6)	-1447(4)	4471(3)	62(1)
C(21)	5536(6)	-680(4)	4098(2)	55(1)
Cl(1)	3167(2)	438(1)	1417(1)	58(1)
Cl(2)	6400(2)	-1102(1)	1424(1)	74(1)
P(1)	6088(1)	475(1)	2848(1)	41(1)

Table A-3.1 Crystal Data and Structure Refinement for 8.

Empirical formula	C ₃₀ H ₂₈ Cl F ₆ P ₃ Ru	
Formula weight	731.95	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 11.5490(6) Å	α = 90°.
	b = 18.2762(10) Å	β = 102.269(2)°.
	c = 14.6245(8) Å	γ = 90°.
Volume	3016.3(3) Å ³	
Z	4	
Density (calculated)	1.612 Mg/m ³	
Absorption coefficient	0.825 mm ⁻¹	
F(000)	1472	
Crystal size	0.25 x 0.25 x 0.25 mm ³	
Theta range for data collection	2.12 to 30.44°.	
Index ranges	-16 ≤ h ≤ 16, -19 ≤ k ≤ 26, -20 ≤ l ≤ 16	
Reflections collected	39932	
Independent reflections	9127 [R(int) = 0.0323]	
Completeness to theta = 30.44°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8203 and 0.8203	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9127 / 0 / 372	
Goodness-of-fit on F ²	1.062	
Final R indices [I > 2σ(I)]	R1 = 0.0318, wR2 = 0.0736	
R indices (all data)	R1 = 0.0403, wR2 = 0.0775	
Largest diff. peak and hole	0.899 and -0.489 e.Å ⁻³	

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad wR2 = \sqrt{\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}}, \quad w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP.$$

Table A-3.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 8. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	4806(1)	2120(1)	4249(1)	16(1)
Cl(1)	5131(1)	1630(1)	2802(1)	24(1)
P(1)	3788(1)	3084(1)	3408(1)	18(1)
P(2)	6415(1)	2828(1)	4155(1)	18(1)
C(1)	3692(2)	2170(1)	5305(2)	35(1)
C(2)	4890(2)	2226(1)	5769(1)	32(1)
C(3)	5694(2)	1662(1)	5652(1)	31(1)
C(4)	5301(2)	1074(1)	5062(2)	30(1)
C(5)	4094(2)	1024(1)	4597(2)	33(1)
C(6)	3281(2)	1554(1)	4734(2)	33(1)
C(7)	2579(2)	2861(1)	2425(1)	21(1)
C(8)	2277(2)	2133(1)	2226(1)	24(1)
C(9)	1335(2)	1955(1)	1486(2)	30(1)
C(10)	714(2)	2503(1)	942(2)	33(1)
C(11)	998(2)	3231(1)	1143(2)	32(1)
C(12)	1915(2)	3413(1)	1884(1)	26(1)
C(13)	3138(2)	3722(1)	4128(1)	22(1)
C(14)	1923(2)	3815(1)	4037(2)	29(1)
C(15)	1487(2)	4283(1)	4636(2)	36(1)
C(16)	2256(2)	4649(1)	5337(2)	38(1)
C(17)	3467(2)	4558(1)	5441(2)	38(1)
C(18)	3910(2)	4100(1)	4838(2)	31(1)
C(19)	4421(2)	4325(1)	2336(1)	27(1)
C(20)	4835(2)	3685(1)	2970(1)	21(1)
C(21)	5984(2)	3557(1)	3318(1)	22(1)
C(22)	7010(2)	3319(1)	5179(1)	24(1)
C(23)	7329(2)	3685(1)	5865(2)	28(1)
C(24)	7684(3)	4152(2)	6690(2)	43(1)
C(25)	7700(2)	2384(1)	3865(1)	21(1)
C(26)	8361(2)	2731(1)	3301(2)	34(1)
C(27)	9364(2)	2390(2)	3111(2)	41(1)
C(28)	9701(2)	1712(1)	3475(2)	36(1)
C(29)	9049(2)	1361(1)	4038(2)	30(1)

C(30)	8049(2)	1695(1)	4235(1)	26(1)
P(3)	8546(1)	297(1)	6837(1)	29(1)
F(1)	8899(2)	509(1)	7911(1)	65(1)
F(2)	9888(1)	196(1)	6780(2)	72(1)
F(3)	8126(2)	107(1)	5751(1)	77(1)
F(4)	7172(1)	401(1)	6884(1)	52(1)
F(5)	8420(2)	-540(1)	7077(2)	64(1)
F(6)	8595(1)	1140(1)	6568(1)	47(1)

Table A-4.1 Crystal Data and Structure Refinement for 10.

Empirical formula	C ₄₀ H ₄₂ Cl ₄ F ₆ N ₃ Pd Ru
Formula weight	1092.93
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 12.5082(4) Å α = 90°. b = 16.1261(5) Å β = 99.573(2)°. c = 21.6743(7) Å γ = 90°.
Volume	4311.0(2) Å ³
Z	4
Density (calculated)	1.684 Mg/m ³
Absorption coefficient	1.184 mm ⁻¹
F(000)	2184
Crystal size	0.30 x 0.20 x 0.15 mm ³
Theta range for data collection	2.08 to 30.52°.
Index ranges	-17 ≤ h ≤ 17, -20 ≤ k ≤ 23, -30 ≤ l ≤ 30
Reflections collected	53722
Independent reflections	13122 [R(int) = 0.0469]
Completeness to theta = 30.52°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8424 and 0.7178
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	13122 / 1 / 528
Goodness-of-fit on F ²	1.033
Final R indices [I > 2σ(I)]	R1 = 0.0429, wR2 = 0.1076
R indices (all data)	R1 = 0.0637, wR2 = 0.1240
Largest diff. peak and hole	1.718 and -1.070 e.Å ⁻³

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad wR2 = \sqrt{\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}}, \quad w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP.$$

Table A-4.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 10. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	2243(1)	9307(1)	4031(1)	24(1)
Ru(1)	1522(1)	6862(1)	2965(1)	23(1)
N(1)	1938(2)	9071(2)	4991(1)	28(1)
Cl(1)	1943(1)	6855(1)	1923(1)	31(1)
Cl(2)	801(1)	10231(1)	3870(1)	58(1)
P(1)	2832(1)	7868(1)	3152(1)	21(1)
P(2)	3039(1)	6057(1)	3255(1)	24(1)
P(3)	2302(1)	2250(1)	694(1)	38(1)
C(1)	464(4)	6052(4)	3442(3)	64(2)
C(2)	21(3)	6065(3)	2802(3)	56(1)
C(3)	-236(3)	6823(3)	2516(2)	49(1)
C(4)	-67(3)	7563(3)	2840(2)	46(1)
C(5)	409(3)	7546(3)	3473(2)	51(1)
C(6)	667(3)	6795(4)	3777(2)	61(2)
C(7)	3043(3)	5012(2)	2937(2)	35(1)
C(8)	2363(3)	4804(3)	2384(2)	39(1)
C(9)	2404(4)	4006(3)	2140(2)	51(1)
C(10)	3113(5)	3428(3)	2445(3)	66(1)
C(11)	3788(5)	3630(3)	2994(3)	71(2)
C(12)	3750(4)	4418(3)	3241(2)	58(1)
C(13)	3455(3)	5920(2)	4099(2)	29(1)
C(14)	2887(3)	5362(3)	4416(2)	45(1)
C(15)	3123(4)	5297(3)	5063(2)	56(1)
C(16)	3918(4)	5791(3)	5394(2)	52(1)
C(17)	4512(3)	6326(3)	5090(2)	41(1)
C(18)	4279(3)	6388(2)	4439(2)	30(1)
C(19)	5186(3)	6138(3)	2927(2)	40(1)
C(20)	4170(3)	6613(2)	3019(1)	25(1)
C(21)	4083(2)	7423(2)	2987(1)	25(1)
C(22)	2621(2)	8848(2)	2760(1)	24(1)
C(23)	2705(3)	8952(2)	2130(2)	30(1)
C(24)	2591(3)	9749(2)	1874(2)	34(1)
C(25)	2418(3)	10409(2)	2242(2)	32(1)

C(26)	2328(2)	10306(2)	2867(2)	28(1)
C(27)	2407(2)	9516(2)	3136(1)	24(1)
C(28)	3136(2)	8199(2)	3969(1)	22(1)
C(29)	3966(2)	8731(2)	4241(1)	22(1)
C(30)	4699(3)	9176(2)	3855(2)	26(1)
C(31)	4412(3)	8669(2)	4930(1)	24(1)
C(32)	5543(3)	8737(2)	5101(2)	29(1)
C(33)	6057(3)	8632(2)	5713(2)	36(1)
C(34)	5459(3)	8487(3)	6179(2)	37(1)
C(35)	4348(3)	8416(2)	6024(2)	35(1)
C(36)	3804(3)	8498(2)	5409(2)	28(1)
C(37)	2592(3)	8379(2)	5314(2)	29(1)
C(38)	2178(3)	9837(2)	5367(2)	38(1)
C(39)	783(3)	8851(3)	4987(2)	38(1)
C(40)	10(30)	1553(16)	9025(13)	140(16)
Cl(3)	-402(7)	743(8)	9434(2)	136(4)
C(40A)	30(20)	1869(13)	9101(9)	65(4)
Cl(3A)	-928(5)	1345(4)	9446(2)	87(2)
Cl(4)	829(2)	1296(2)	8603(1)	143(1)
F(1)	2723(7)	1362(3)	829(3)	187(3)
F(2)	3435(4)	2584(4)	974(2)	155(3)
F(3)	1942(8)	3121(4)	616(3)	234(5)
F(4)	1215(4)	1889(6)	434(2)	206(4)
F(5)	2604(3)	2231(3)	23(2)	104(1)
F(6)	2020(2)	2237(2)	1387(1)	63(1)

Table A-5.1 Crystal Data and Structure Refinement for 13.

Empirical formula	C ₂₂ H ₂₆ Cl F ₆ N ₅ P ₂ Ru	
Formula weight	672.94	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.5540(3) Å	α = 95.094(2)°.
	b = 12.7318(5) Å	β = 92.713(2)°.
	c = 14.1568(5) Å	γ = 108.771(2)°.
Volume	1449.30(9) Å ³	
Z	2	
Density (calculated)	1.542 Mg/m ³	
Absorption coefficient	0.802 mm ⁻¹	
F(000)	676	
Crystal size	0.30 x 0.30 x 0.20 mm ³	
Theta range for data collection	2.35 to 30.54°.	
Index ranges	-12 ≤ h ≤ 12, -18 ≤ k ≤ 18, -20 ≤ l ≤ 20	
Reflections collected	29887	
Independent reflections	8772 [R(int) = 0.0252]	
Completeness to theta = 30.54°	99.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8560 and 0.7948	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8772 / 0 / 341	
Goodness-of-fit on F ²	1.055	
Final R indices [I > 2σ(I)]	R1 = 0.0300, wR2 = 0.0780	
R indices (all data)	R1 = 0.0362, wR2 = 0.0839	
Largest diff. peak and hole	0.736 and -0.583 e.Å ⁻³	

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad wR2 = \sqrt{\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}}, \quad w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP.$$

Table A-5.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 13. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	5524(1)	7265(1)	6375(1)	20(1)
Cl(1)	3465(1)	6660(1)	5052(1)	29(1)
N(1)	4888(2)	5699(1)	6750(1)	27(1)
N(2)	6247(2)	8832(1)	5991(1)	24(1)
N(3)	7331(2)	7779(1)	7449(1)	26(1)
N(4)	7211(2)	6848(1)	5484(1)	26(1)
P(1)	3658(1)	7640(1)	7312(1)	22(1)
C(1)	2946(2)	8788(2)	7048(1)	25(1)
C(2)	3999(3)	9871(2)	7295(2)	39(1)
C(3)	3515(4)	10765(2)	7082(2)	52(1)
C(4)	1975(4)	10583(2)	6630(2)	56(1)
C(5)	904(3)	9510(2)	6386(2)	51(1)
C(6)	1385(3)	8610(2)	6595(2)	37(1)
C(7)	1782(3)	6540(2)	7327(2)	30(1)
C(8)	454(3)	5834(2)	7306(2)	33(1)
C(9)	-1165(3)	4988(2)	7292(2)	46(1)
C(10)	4342(3)	8001(2)	8523(1)	32(1)
C(11)	4948(3)	8305(3)	9315(2)	45(1)
C(12)	5677(5)	8655(4)	10296(2)	78(1)
C(13)	4637(3)	4825(2)	6959(2)	33(1)
C(14)	4335(4)	3695(2)	7209(2)	50(1)
C(15)	6662(3)	9740(2)	5836(1)	29(1)
C(16)	7156(4)	10907(2)	5664(2)	46(1)
C(17)	8323(3)	8100(2)	8058(2)	33(1)
C(18)	9603(4)	8529(3)	8842(2)	61(1)
C(19)	8051(2)	6538(2)	5032(1)	27(1)
C(20)	9147(3)	6135(2)	4454(2)	36(1)
C(21)	7036(6)	5182(4)	-236(3)	87(1)
C(22)	7546(8)	4623(5)	466(4)	122(2)
F(1)	-69(3)	7451(2)	2427(2)	85(1)
F(2)	2527(2)	7889(2)	2011(1)	67(1)
F(3)	463(4)	7008(2)	908(2)	119(1)
F(4)	1855(3)	8773(3)	804(2)	98(1)

F(5)	-747(3)	8302(2)	1226(2)	84(1)
F(6)	1385(3)	9230(2)	2287(2)	81(1)
N(5)	6645(7)	5610(5)	-818(3)	132(2)
P(2)	890(1)	8093(1)	1611(1)	45(1)

Table A-6.1 Crystal Data and Structure Refinement for 14.

Empirical formula	C ₃₀ H ₃₁ Cl F ₆ N ₃ P ₃ Ru	
Formula weight	777.01	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 8.5677(6) Å	α = 90°.
	b = 17.2487(12) Å	β = 92.248(5)°.
	c = 23.8966(18) Å	γ = 90°.
Volume	3528.8(4) Å ³	
Z	4	
Density (calculated)	1.463 Mg/m ³	
Absorption coefficient	0.712 mm ⁻¹	
F(000)	1568	
Crystal size	0.30 x 0.06 x 0.06 mm ³	
Theta range for data collection	2.36 to 25.05°.	
Index ranges	-10 ≤ h ≤ 10, -20 ≤ k ≤ 20, -28 ≤ l ≤ 28	
Reflections collected	21590	
Independent reflections	6213 [R(int) = 0.0861]	
Completeness to theta = 25.05°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9585 and 0.8148	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6213 / 78 / 406	
Goodness-of-fit on F ²	1.124	
Final R indices [I > 2σ(I)]	R1 = 0.0864, wR2 = 0.1854	
R indices (all data)	R1 = 0.1342, wR2 = 0.2082	
Largest diff. peak and hole	0.683 and -0.972 e.Å ⁻³	

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad wR2 = \sqrt{\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}}, \quad w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP.$$

Table A-6.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 14. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	723(1)	6872(1)	1552(1)	42(1)
N(1)	-1420(11)	6432(5)	1407(4)	58(2)
N(2)	1597(9)	6028(5)	1062(3)	48(2)
N(3)	2834(11)	7327(4)	1742(3)	53(2)
Cl(1)	-457(3)	7839(1)	2115(1)	58(1)
P(1)	387(3)	7663(1)	754(1)	43(1)
P(2)	1004(4)	6077(2)	2348(1)	59(1)
C(1)	1283(11)	8628(6)	714(4)	53(3)
C(2)	1742(14)	9042(6)	1179(5)	67(3)
C(3)	2432(17)	9749(7)	1127(7)	95(5)
C(4)	2670(20)	10072(8)	626(9)	118(6)
C(5)	2200(20)	9662(9)	140(8)	118(6)
C(6)	1508(16)	8956(8)	185(5)	85(4)
C(7)	-1639(13)	7799(6)	520(4)	59(3)
C(8)	-2548(15)	8365(7)	722(5)	78(4)
C(9)	-4192(18)	8394(10)	537(7)	102(5)
C(10)	-4720(20)	7862(12)	175(8)	130(6)
C(11)	-3830(20)	7307(13)	-29(9)	178(8)
C(12)	-2266(18)	7285(10)	139(7)	129(6)
C(13)	-4299(17)	5930(9)	1278(10)	175(11)
C(14)	-2671(17)	6201(7)	1354(7)	95(5)
C(15)	2358(16)	4834(7)	473(5)	83(4)
C(16)	1930(12)	5508(6)	803(4)	54(3)
C(17)	5394(16)	7987(9)	2150(7)	122(6)
C(18)	3972(15)	7611(6)	1915(5)	66(3)
C(19)	1889(15)	5178(7)	2228(5)	71(3)
C(20)	2410(15)	4578(6)	2069(5)	67(3)
C(21)	3045(17)	3843(7)	1880(6)	93(5)
C(22)	2147(19)	6463(7)	2909(5)	91(5)
C(23)	2870(30)	6735(8)	3288(7)	135(8)
C(24)	3660(30)	7031(11)	3795(8)	210(13)

C(25)	-714(18)	5785(6)	2695(5)	85(4)
C(26)	-1542(18)	5150(7)	2537(7)	99(5)
C(27)	-2970(30)	4951(10)	2794(10)	158(7)
C(28)	-3410(30)	5403(13)	3237(12)	201(9)
C(29)	-2620(30)	6028(15)	3380(11)	217(10)
C(30)	-1230(30)	6251(11)	3135(8)	165(8)
F(1)	8232(15)	4628(5)	923(5)	178(5)
F(2)	6460(30)	3882(13)	1264(13)	382(17)
F(3)	6650(20)	3898(9)	455(9)	274(11)
F(4)	7347(18)	2873(6)	910(6)	215(7)
F(5)	8790(30)	3621(8)	1418(6)	293(12)
F(6)	9050(20)	3624(8)	517(7)	248(8)
P(3)	7796(6)	3735(2)	934(2)	94(1)

Table A-7.1 Crystal Data and Structure Refinement for 16.

Empirical formula	C ₃₁ H ₃₅ Cl ₃ N O P Pd Ru
Formula weight	782.39
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 9.2914(2) Å α = 90°. b = 13.1116(4) Å β = 90°. c = 25.8438(7) Å γ = 90°.
Volume	3148.42(15) Å ³
Z	4
Density (calculated)	1.651 Mg/m ³
Absorption coefficient	1.382 mm ⁻¹
F(000)	1568
Crystal size	0.10 x 0.10 x 0.05 mm ³
Theta range for data collection	1.74 to 30.53°
Index ranges	-13 ≤ h ≤ 11, -18 ≤ k ≤ 18, -36 ≤ l ≤ 36
Reflections collected	50695
Independent reflections	9596 [R(int) = 0.0350]
Completeness to theta = 30.53°	99.8 %
Absorption correction	None
Max. and min. transmission	0.9341 and 0.8742
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	9596 / 0 / 364
Goodness-of-fit on F ²	1.114
Final R indices [I > 2σ(I)]	R1 = 0.0218, wR2 = 0.0492
R indices (all data)	R1 = 0.0265, wR2 = 0.0582
Absolute structure parameter	-0.017(17)
Largest diff. peak and hole	0.523 and -0.548 e.Å ⁻³

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad wR2 = \sqrt{\{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}}, \quad w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP.$$

Table A-7.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 16. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	1026(1)	3782(1)	971(1)	18(1)
Ru(1)	1272(1)	4926(1)	2402(1)	17(1)
Cl(1)	132(1)	3736(1)	1822(1)	19(1)
Cl(2)	-572(1)	6134(1)	2172(1)	27(1)
Cl(3)	363(1)	1998(1)	943(1)	37(1)
N(1)	2032(2)	3848(2)	227(1)	25(1)
O(1)	2710(3)	1237(2)	1815(2)	55(1)
P(1)	2467(1)	5466(1)	1657(1)	17(1)
C(1)	-464(3)	5581(2)	423(1)	24(1)
C(2)	-1932(3)	5818(2)	458(1)	33(1)
C(3)	-2896(4)	5467(3)	86(1)	45(1)
C(4)	-2414(4)	4900(3)	-323(1)	47(1)
C(5)	-967(4)	4685(2)	-369(1)	38(1)
C(6)	24(3)	5018(2)	-2(1)	26(1)
C(7)	1631(3)	4824(2)	-55(1)	27(1)
C(8)	2162(4)	4866(2)	-615(1)	43(1)
C(9)	1649(4)	2936(2)	-90(1)	38(1)
C(10)	3611(3)	3824(3)	315(1)	38(1)
C(11)	406(3)	7089(2)	934(1)	33(1)
C(12)	519(3)	5952(2)	840(1)	21(1)
C(13)	1361(3)	5267(2)	1087(1)	19(1)
C(14)	3109(3)	6774(2)	1641(1)	22(1)
C(15)	2765(3)	7461(2)	2034(1)	26(1)
C(16)	3096(3)	8489(2)	1984(1)	31(1)
C(17)	3767(3)	8839(2)	1537(1)	36(1)
C(18)	4131(3)	8162(2)	1147(1)	36(1)
C(19)	3802(3)	7141(2)	1196(1)	28(1)
C(20)	4097(3)	4689(2)	1578(1)	20(1)
C(21)	3969(3)	3627(2)	1590(1)	24(1)
C(22)	5173(3)	3010(2)	1541(1)	27(1)
C(23)	6527(3)	3445(2)	1490(1)	32(1)

C(24)	6673(3)	4485(2)	1505(1)	34(1)
C(25)	5471(3)	5110(2)	1547(1)	26(1)
C(26)	3252(3)	4439(2)	2782(1)	32(1)
C(27)	2241(3)	3673(2)	2833(1)	32(1)
C(28)	892(3)	3870(2)	3074(1)	32(1)
C(29)	560(3)	4849(2)	3234(1)	32(1)
C(30)	1555(3)	5657(2)	3149(1)	34(1)
C(31)	2920(3)	5447(2)	2942(1)	34(1)

Table A-8.1 Crystal Data and Structure Refinement for 20.

Empirical formula	C ₃₆ H ₄₀ Cl ₂ N ₂ O P Pd ₂	
Formula weight	831.37	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 12.5912(3) Å	α = 90°.
	b = 10.5421(2) Å	β = 93.0070(10)°.
	c = 26.2042(5) Å	γ = 90°.
Volume	3473.50(12) Å ³	
Z	4	
Density (calculated)	1.590 Mg/m ³	
Absorption coefficient	1.266 mm ⁻¹	
F(000)	1676	
Crystal size	0.32 x 0.30 x 0.16 mm ³	
Theta range for data collection	1.56 to 30.64°.	
Index ranges	-18 ≤ h ≤ 18, -15 ≤ k ≤ 15, -37 ≤ l ≤ 37	
Reflections collected	46595	
Independent reflections	10666 [R(int) = 0.0368]	
Completeness to theta = 30.64°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8231 and 0.6874	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	10666 / 0 / 403	
Goodness-of-fit on F ²	1.178	
Final R indices [I > 2σ(I)]	R1 = 0.0267, wR2 = 0.0742	
R indices (all data)	R1 = 0.0395, wR2 = 0.1000	
Largest diff. peak and hole	0.885 and -1.052 e.Å ⁻³	

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad wR2 = \sqrt{\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}}, \quad w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP.$$

Table A-8.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 20. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	7816(1)	6245(1)	4171(1)	19(1)
Pd(2)	6229(1)	6860(1)	3197(1)	16(1)
C(1)	8564(2)	7164(2)	4754(1)	26(1)
C(2)	9474(3)	7919(3)	4760(1)	33(1)
C(3)	9908(3)	8419(3)	5216(1)	44(1)
C(4)	9459(3)	8152(3)	5670(1)	52(1)
C(5)	8572(3)	7393(3)	5675(1)	44(1)
C(6)	8125(3)	6896(3)	5224(1)	32(1)
C(7)	7175(3)	6029(3)	5212(1)	38(1)
C(8)	8101(3)	4148(3)	4928(1)	37(1)
C(9)	6242(3)	4455(3)	4683(1)	42(1)
C(10)	9849(2)	7027(2)	3480(1)	20(1)
C(11)	10685(2)	7889(2)	3514(1)	29(1)
C(12)	11728(2)	7472(3)	3478(1)	39(1)
C(13)	11937(2)	6205(3)	3405(1)	40(1)
C(14)	11117(2)	5351(3)	3373(1)	37(1)
C(15)	10077(2)	5742(2)	3418(1)	29(1)
C(16)	8357(2)	9157(2)	3575(1)	20(1)
C(17)	8608(2)	9900(2)	3158(1)	26(1)
C(18)	8395(2)	11191(2)	3152(1)	33(1)
C(19)	7935(3)	11748(2)	3562(1)	38(1)
C(20)	7684(2)	11028(2)	3979(1)	34(1)
C(21)	7893(2)	9734(2)	3987(1)	26(1)
C(22)	7681(2)	7146(2)	2953(1)	17(1)
C(23)	7979(2)	7046(2)	2472(1)	20(1)
C(24)	9116(2)	7025(3)	2306(1)	28(1)
C(25)	7165(2)	6926(2)	2040(1)	20(1)
C(26)	7286(2)	5993(2)	1672(1)	26(1)
C(27)	6611(2)	5912(3)	1239(1)	32(1)
C(28)	5801(2)	6798(3)	1163(1)	31(1)
C(29)	5673(2)	7736(3)	1524(1)	28(1)

C(30)	6330(2)	7807(2)	1968(1)	22(1)
C(31)	6167(2)	8840(2)	2351(1)	24(1)
C(32)	4454(2)	8082(3)	2608(1)	31(1)
C(33)	5484(2)	9511(2)	3154(1)	30(1)
C(34)	6090(2)	5062(3)	-13(1)	32(1)
C(35)	5632(2)	4096(3)	259(1)	30(1)
C(36)	4532(2)	4037(3)	274(1)	32(1)
Cl(1)	6955(1)	4937(1)	3509(1)	24(1)
Cl(2)	4670(1)	6472(1)	3689(1)	29(1)
N(1)	7273(2)	5111(2)	4786(1)	29(1)
N(2)	5555(2)	8419(2)	2797(1)	22(1)
O(1)	6304(2)	3255(2)	510(1)	37(1)
P(1)	8457(1)	7437(1)	3544(1)	16(1)

Table A-9.1 Crystal Data and Structure Refinement for ($R_{Ru}R_P S_C$)-22.

Empirical formula	C ₂₉ H ₃₂ Cl ₆ N P Pd Ru	
Formula weight	845.70	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 10.0546(4) Å	$\alpha = 90^\circ$.
	b = 13.1269(5) Å	$\beta = 110.007(2)^\circ$.
	c = 13.0716(5) Å	$\gamma = 90^\circ$.
Volume	1621.15(11) Å ³	
Z	2	
Density (calculated)	1.732 Mg/m ³	
Absorption coefficient	1.585 mm ⁻¹	
F(000)	840	
Crystal size	0.15 x 0.15 x 0.08 mm ³	
Theta range for data collection	2.16 to 30.51°	
Index ranges	-14 ≤ h ≤ 14, -18 ≤ k ≤ 18, -18 ≤ l ≤ 18	
Reflections collected	40668	
Independent reflections	9838 [R(int) = 0.0242]	
Completeness to theta = 30.51°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8836 and 0.7969	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9838 / 1 / 357	
Goodness-of-fit on F ²	1.032	
Final R indices [I > 2σ(I)]	R1 = 0.0200, wR2 = 0.0464	
R indices (all data)	R1 = 0.0216, wR2 = 0.0471	
Absolute structure parameter	-0.025(13)	
Largest diff. peak and hole	0.921 and -0.812 e.Å ⁻³	

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad wR2 = \sqrt{\{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}}, \quad w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP.$$

Table A-9.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ($R_{Ru}R_P S_C$)-22. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	3273(1)	1907(1)	6445(1)	17(1)
Ru(1)	6330(1)	3098(1)	5501(1)	19(1)
Cl(1)	7597(1)	1631(1)	6420(1)	34(1)
Cl(2)	4227(1)	2084(1)	5053(1)	23(1)
Cl(3)	1063(1)	1651(1)	4943(1)	27(1)
N(1)	2234(2)	1773(1)	7602(1)	22(1)
P(1)	5825(1)	3365(1)	7096(1)	20(1)
C(1)	8122(2)	4069(2)	5555(2)	35(1)
C(2)	8009(3)	3307(2)	4774(2)	39(1)
C(3)	6734(3)	3143(2)	3916(2)	38(1)
C(4)	5542(3)	3753(2)	3857(2)	34(1)
C(5)	5642(2)	4544(2)	4595(2)	31(1)
C(6)	6935(2)	4686(2)	5469(2)	32(1)
C(7)	7327(2)	3904(2)	8091(2)	28(1)
C(8)	8416(2)	4282(2)	8642(2)	34(1)
C(9)	9792(3)	4689(3)	9332(3)	60(1)
C(10)	4451(2)	4298(2)	7039(2)	22(1)
C(11)	4477(3)	4819(2)	7976(2)	33(1)
C(12)	3362(3)	5466(2)	7952(2)	42(1)
C(13)	2237(3)	5602(2)	6993(2)	39(1)
C(14)	2199(3)	5095(2)	6060(2)	34(1)
C(15)	3305(2)	4444(2)	6077(2)	27(1)
C(16)	5190(2)	2217(1)	7557(2)	20(1)
C(17)	5939(2)	1596(2)	8371(2)	24(1)
C(18)	7479(2)	1737(2)	9087(2)	38(1)
C(19)	5304(2)	638(2)	8617(2)	23(1)
C(20)	6043(3)	-284(2)	8694(2)	32(1)
C(21)	5524(3)	-1182(2)	8960(2)	39(1)
C(22)	4276(3)	-1190(2)	9180(2)	39(1)
C(23)	3542(3)	-289(2)	9126(2)	31(1)
C(24)	4023(2)	632(2)	8834(2)	22(1)

C(25)	3209(2)	1607(2)	8772(2)	24(1)
C(26)	2442(3)	1657(2)	9604(2)	37(1)
C(27)	1176(2)	922(2)	7262(2)	29(1)
C(28)	1449(3)	2749(2)	7513(2)	34(1)
C(29)	1029(2)	2951(2)	2746(2)	35(1)
Cl(4)	1635(1)	4213(1)	3007(1)	39(1)
Cl(5)	1946(1)	2292(1)	2021(1)	76(1)
Cl(6)	-808(1)	2950(1)	2046(1)	73(1)

Table A-10.1 Crystal Data and Structure Refinement for ($R_{Ru}S_P S_C$)-22.

Empirical formula	C _{28.50} H ₃₂ Cl ₄ N P Pd Ru
Formula weight	768.79
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 8.7910(2) Å α = 90°. b = 13.6179(4) Å β = 90°. c = 26.1332(7) Å γ = 90°.
Volume	3128.53(14) Å ³
Z	4
Density (calculated)	1.632 Mg/m ³
Absorption coefficient	1.469 mm ⁻¹
F(000)	1532
Crystal size	0.15 x 0.10 x 0.06 mm ³
Theta range for data collection	2.16 to 30.53°.
Index ranges	-12 ≤ h ≤ 12, -19 ≤ k ≤ 19, -37 ≤ l ≤ 37
Reflections collected	66719
Independent reflections	9476 [R(int) = 0.0544]
Completeness to theta = 30.53°	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9170 and 0.8097
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	9476 / 39 / 336
Goodness-of-fit on F ²	1.028
Final R indices [I > 2σ(I)]	R1 = 0.0504, wR2 = 0.1203
R indices (all data)	R1 = 0.0835, wR2 = 0.1424
Absolute structure parameter	0.00(5)
Largest diff. peak and hole	1.007 and -1.232 e.Å ⁻³

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad wR2 = \sqrt{\{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}}, \quad w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP.$$

Table A-10.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ($R_{Ru}S_P S_C$)-22. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	5727(1)	6140(1)	3990(1)	45(1)
Ru(1)	6147(1)	5044(1)	2575(1)	76(1)
Cl(1)	3950(4)	4048(2)	2743(1)	98(1)
Cl(2)	5036(2)	6268(1)	3126(1)	61(1)
Cl(3)	5356(5)	7888(1)	4017(1)	132(1)
N(1)	6542(6)	6070(4)	4759(2)	54(1)
P(1)	7106(2)	4458(1)	3344(1)	53(1)
C(1)	5776(12)	5732(9)	1807(3)	138(5)
C(2)	5878(15)	4720(9)	1749(3)	182(7)
C(3)	7118(19)	4214(6)	1947(4)	201(9)
C(4)	8258(12)	4722(12)	2204(4)	201(9)
C(5)	8157(12)	5734(11)	2263(3)	186(7)
C(6)	6916(16)	6239(5)	2064(4)	136(5)
C(7)	8758(8)	5127(5)	3502(4)	74(2)
C(8)	9902(11)	5572(8)	3562(5)	104(4)
C(9)	11320(13)	6103(12)	3643(7)	178(8)
C(10)	7815(9)	3205(5)	3357(3)	62(2)
C(11)	8743(10)	2902(6)	3760(4)	81(2)
C(12)	9210(14)	1921(7)	3784(5)	111(4)
C(13)	8742(13)	1260(6)	3427(4)	103(4)
C(14)	7871(14)	1549(6)	3018(4)	99(3)
C(15)	7398(12)	2526(5)	2984(3)	81(3)
C(16)	5882(6)	4688(3)	3883(2)	42(1)
C(17)	4966(7)	4042(4)	4120(2)	46(1)
C(18)	4805(10)	2949(5)	3989(3)	77(2)
C(19)	3974(6)	4357(4)	4548(2)	44(1)
C(20)	2397(7)	4114(5)	4534(3)	59(2)
C(21)	1447(9)	4385(7)	4922(3)	82(2)
C(22)	1947(10)	4885(8)	5330(3)	87(3)
C(23)	3517(10)	5113(6)	5360(3)	74(2)
C(24)	4544(6)	4858(5)	4975(2)	48(1)

C(25)	6227(7)	5089(4)	5011(2)	49(1)
C(26)	6860(10)	5000(7)	5555(3)	76(2)
C(27)	8240(9)	6197(7)	4703(4)	91(3)
C(28)	5938(14)	6876(6)	5074(3)	91(3)
C(29)	8266(17)	8076(19)	3099(5)	125(10)
Cl(4)	9153(13)	8298(6)	3571(4)	190(5)
Cl(5)	9186(9)	7893(8)	2528(3)	177(4)

Table A-11.1 Crystal Data and Structure Refinement for ($R_{Ru}S_P$)-23/($S_{Ru}R_P$)-23.

Empirical formula	C ₂₈ H ₃₁ Cl ₅ N P Pd Ru	
Formula weight	797.23	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 15.5945(6) Å	α = 90°.
	b = 12.6641(5) Å	β = 102.418(2)°.
	c = 15.7896(6) Å	γ = 90°.
Volume	3045.3(2) Å ³	
Z	4	
Density (calculated)	1.739 Mg/m ³	
Absorption coefficient	1.597 mm ⁻¹	
F(000)	1584	
Crystal size	0.25 x 0.15 x 0.10 mm ³	
Theta range for data collection	2.07 to 30.67°.	
Index ranges	-22 ≤ h ≤ 22, -18 ≤ k ≤ 18, -22 ≤ l ≤ 22	
Reflections collected	69524	
Independent reflections	9317 [R(int) = 0.0272]	
Completeness to theta = 30.67°	98.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8566 and 0.6909	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9317 / 0 / 338	
Goodness-of-fit on F ²	1.045	
Final R indices [I > 2σ(I)]	R1 = 0.0256, wR2 = 0.0614	
R indices (all data)	R1 = 0.0313, wR2 = 0.0655	
Largest diff. peak and hole	0.989 and -0.650 e.Å ⁻³	

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad wR2 = \sqrt{\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}}, \quad w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP.$$

Table A-11.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $(R_{\text{Ru}}S_{\text{P}})\text{-23}/(S_{\text{Ru}}R_{\text{P}})\text{-23}$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	7009(1)	7895(1)	1156(1)	22(1)
Ru(1)	6700(1)	5506(1)	-559(1)	27(1)
Cl(1)	5769(1)	6683(1)	-1551(1)	40(1)
Cl(2)	6213(1)	6389(1)	602(1)	36(1)
Cl(3)	6623(1)	7440(1)	2508(1)	46(1)
Cl(4)	5487(1)	4786(1)	6142(1)	72(1)
Cl(5)	6385(1)	6666(1)	5705(1)	80(1)
N(1)	7711(1)	9242(2)	1700(1)	31(1)
P(1)	7744(1)	6856(1)	-303(1)	22(1)
C(1)	7619(2)	4236(2)	-123(3)	84(2)
C(2)	6856(3)	4052(2)	187(2)	64(1)
C(3)	6056(2)	3972(2)	-372(3)	67(1)
C(4)	5959(3)	4106(2)	-1199(3)	72(1)
C(5)	6640(4)	4327(2)	-1562(2)	78(1)
C(6)	7507(3)	4394(2)	-1067(4)	94(2)
C(7)	8551(1)	6545(2)	637(1)	31(1)
C(8)	9082(2)	6289(2)	1261(2)	39(1)
C(9)	9752(2)	5989(3)	2019(2)	64(1)
C(10)	8419(1)	6925(2)	-1114(1)	28(1)
C(11)	9328(2)	7129(2)	-866(2)	37(1)
C(12)	9838(2)	7165(2)	-1493(2)	42(1)
C(13)	9451(2)	6992(2)	-2359(2)	39(1)
C(14)	8572(2)	6778(2)	-2601(1)	35(1)
C(15)	8060(2)	6739(2)	-1982(1)	32(1)
C(16)	7303(1)	8100(1)	-14(1)	21(1)
C(17)	7035(1)	8912(1)	-557(1)	22(1)
C(18)	7123(2)	8985(2)	-1493(1)	31(1)
C(19)	6598(1)	9843(1)	-257(1)	23(1)
C(20)	5791(1)	10194(2)	-756(1)	30(1)
C(21)	5353(2)	11050(2)	-495(2)	36(1)
C(22)	5725(2)	11594(2)	251(2)	39(1)

C(23)	6540(2)	11290(2)	730(2)	36(1)
C(24)	6978(1)	10406(2)	493(1)	27(1)
C(25)	7839(1)	10060(2)	1048(1)	30(1)
C(26)	7255(2)	9770(2)	2334(2)	47(1)
C(27)	8589(2)	8883(2)	2178(2)	48(1)
C(28)	5503(2)	6165(3)	6125(2)	58(1)

Table A-12.1 Crystal Data and Structure Refinement for 25.

Empirical formula	C ₂₇ H ₃₀ Cl ₂ N O P Pd Ru	
Formula weight	693.86	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 13.8455(6) Å	α = 90°.
	b = 9.4914(4) Å	β = 105.924(2)°.
	c = 21.3557(8) Å	γ = 90°.
Volume	2698.73(19) Å ³	
Z	4	
Density (calculated)	1.708 Mg/m ³	
Absorption coefficient	1.504 mm ⁻¹	
F(000)	1384	
Crystal size	0.20 x 0.20 x 0.06 mm ³	
Theta range for data collection	1.98 to 28.50°.	
Index ranges	-18 ≤ h ≤ 18, -12 ≤ k ≤ 12, -28 ≤ l ≤ 28	
Reflections collected	28700	
Independent reflections	6733 [R(int) = 0.0318]	
Completeness to theta = 28.50°	98.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9152 and 0.7530	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6733 / 36 / 311	
Goodness-of-fit on F ²	1.126	
Final R indices [I > 2σ(I)]	R1 = 0.0278, wR2 = 0.0695	
R indices (all data)	R1 = 0.0340, wR2 = 0.0779	
Largest diff. peak and hole	0.888 and -1.291 e.Å ⁻³	

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR2 = \sqrt{\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}}, w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP.$$

Table A-12.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 25. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	3515(1)	966(1)	855(1)	17(1)
Ru(1)	5929(1)	3374(1)	1653(1)	18(1)
C(1)	7052(5)	3593(6)	1066(3)	65(2)
C(2)	7216(3)	4678(6)	1500(3)	52(1)
C(3)	6411(4)	5537(4)	1551(2)	41(1)
C(4)	5469(3)	5335(5)	1138(2)	44(1)
C(5)	5293(4)	4229(6)	694(2)	53(1)
C(6)	6064(6)	3328(5)	670(2)	63(2)
C(7)	5562(3)	-1015(4)	2135(2)	35(1)
C(8)	5335(3)	474(3)	1905(2)	23(1)
C(9)	4364(2)	1062(3)	1860(1)	19(1)
C(10)	4059(2)	3771(3)	2500(2)	21(1)
C(11)	3278(3)	3231(4)	2717(2)	27(1)
C(12)	2995(3)	3894(4)	3219(2)	35(1)
C(13)	3492(3)	5101(5)	3500(2)	37(1)
C(14)	4267(3)	5650(4)	3286(2)	37(1)
C(15)	4561(3)	4988(4)	2784(2)	29(1)
C(16)	3285(2)	2948(3)	1114(1)	17(1)
C(17)	2522(3)	3851(3)	968(2)	21(1)
C(18)	2580(3)	5319(4)	1261(2)	33(1)
C(19)	1514(2)	3475(3)	522(2)	21(1)
C(20)	661(3)	3745(4)	733(2)	30(1)
C(21)	-292(3)	3351(4)	361(2)	36(1)
C(22)	-417(3)	2710(4)	-237(2)	40(1)
C(23)	414(3)	2485(4)	-464(2)	36(1)
C(24)	1375(3)	2836(3)	-90(2)	25(1)
C(25)	2255(3)	2564(4)	-360(2)	27(1)
C(26)	2008(3)	25(4)	-398(2)	31(1)
C(27)	3554(3)	1018(4)	-506(2)	30(1)
Cl(1)	3840(1)	-1509(1)	715(1)	28(1)
Cl(2)	6632(1)	3254(1)	2811(1)	29(1)

N(1)	2760(2)	1166(3)	-163(1)	23(1)
O(1)	6027(2)	1167(2)	1768(1)	25(1)
P(1)	4367(1)	2959(1)	1804(1)	16(1)

Table A-13.1 Crystal Data and Structure Refinement for ($R_{Ru}R_PScSc$)-30.

Empirical formula	C ₂₈ H ₃₂ Cl ₂ N O P Pd Ru	
Formula weight	707.89	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 10.2816(2) Å	α = 90°.
	b = 13.3428(3) Å	β = 108.8250(10)°.
	c = 10.4877(2) Å	γ = 90°.
Volume	1361.80(5) Å ³	
Z	2	
Density (calculated)	1.726 Mg/m ³	
Absorption coefficient	1.492 mm ⁻¹	
F(000)	708	
Crystal size	0.30 x 0.30 x 0.12 mm ³	
Theta range for data collection	2.05 to 41.35°.	
Index ranges	-19 ≤ h ≤ 17, -17 ≤ k ≤ 24, -18 ≤ l ≤ 19	
Reflections collected	68676	
Independent reflections	14317 [R(int) = 0.0239]	
Completeness to theta = 41.35°	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8412 and 0.6631	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	14317 / 1 / 321	
Goodness-of-fit on F ²	1.084	
Final R indices [I > 2σ(I)]	R1 = 0.0230, wR2 = 0.0489	
R indices (all data)	R1 = 0.0272, wR2 = 0.0546	
Absolute structure parameter	-0.007(12)	
Largest diff. peak and hole	0.913 and -0.730 e.Å ⁻³	

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad wR2 = \sqrt{\{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}}, \quad w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP.$$

Table A-13.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $(R_{Ru}R_P S_C S_C)$ -30. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	9281(1)	3660(1)	8932(1)	18(1)
Ru(1)	5653(1)	2490(1)	6802(1)	18(1)
C(1)	4252(3)	1150(2)	6141(2)	43(1)
C(2)	3841(2)	1793(2)	7027(3)	41(1)
C(3)	4764(3)	2008(2)	8303(2)	38(1)
C(4)	6153(3)	1652(2)	8674(2)	37(1)
C(5)	6561(2)	1097(2)	7747(3)	40(1)
C(6)	5599(3)	808(2)	6495(3)	43(1)
C(7)	8563(2)	3828(2)	5125(2)	34(1)
C(8)	7815(2)	3577(1)	6087(1)	21(1)
C(9)	7816(2)	4256(1)	7147(2)	19(1)
C(10)	5245(2)	5016(1)	7612(2)	19(1)
C(11)	5635(2)	5995(1)	7474(2)	28(1)
C(12)	4719(2)	6778(2)	7382(3)	37(1)
C(13)	3418(2)	6589(2)	7439(2)	33(1)
C(14)	3017(2)	5622(2)	7566(2)	30(1)
C(15)	3917(2)	4826(1)	7634(2)	26(1)
C(16)	7661(1)	3982(1)	9506(2)	17(1)
C(17)	7527(1)	4310(1)	10665(2)	18(1)
C(18)	6150(2)	4492(2)	10863(2)	29(1)
C(19)	8749(2)	4591(1)	11827(2)	19(1)
C(20)	8783(2)	5562(1)	12341(2)	24(1)
C(21)	9901(2)	5910(2)	13392(2)	31(1)
C(22)	10979(2)	5265(2)	13979(2)	33(1)
C(23)	10943(2)	4300(2)	13505(2)	29(1)
C(24)	9856(2)	3947(1)	12412(2)	21(1)
C(25)	9858(2)	2895(1)	11890(2)	23(1)
C(26)	10501(2)	2137(2)	13015(2)	35(1)
C(27)	11911(2)	3264(2)	11225(2)	32(1)
C(28)	10478(2)	1832(2)	10274(2)	34(1)
Cl(1)	11098(1)	3414(1)	7954(1)	33(1)

Cl(2)	4331(1)	3476(1)	4948(1)	28(1)
N(1)	10481(1)	2877(1)	10759(2)	23(1)
O(1)	7170(1)	2759(1)	5906(1)	23(1)
P(1)	6467(1)	3985(1)	7846(1)	16(1)

Table A-14.1 Crystal Data and Structure Refinement for 32.

Empirical formula	C ₃₃ H ₃₆ Cl ₃ N ₂ P Pd Ru	
Formula weight	805.43	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.3445(3) Å	α = 84.9040(10)°.
	b = 11.0867(3) Å	β = 81.888(2)°.
	c = 16.7001(5) Å	γ = 70.0240(10)°.
Volume	1608.23(8) Å ³	
Z	2	
Density (calculated)	1.663 Mg/m ³	
Absorption coefficient	1.354 mm ⁻¹	
F(000)	808	
Crystal size	0.30 x 0.20 x 0.16 mm ³	
Theta range for data collection	1.23 to 31.12°.	
Index ranges	-13 ≤ h ≤ 13, -16 ≤ k ≤ 16, -23 ≤ l ≤ 24	
Reflections collected	37533	
Independent reflections	10276 [R(int) = 0.0300]	
Completeness to theta = 31.12°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8125 and 0.6869	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	10276 / 0 / 373	
Goodness-of-fit on F ²	1.106	
Final R indices [I > 2σ(I)]	R1 = 0.0270, wR2 = 0.0652	
R indices (all data)	R1 = 0.0377, wR2 = 0.0802	
Largest diff. peak and hole	0.583 and -0.672 e.Å ⁻³	

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad wR2 = \sqrt{\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}}, \quad w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP.$$

Table A-14.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 32. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	5290(1)	3887(1)	2419(1)	16(1)
Ru(1)	7568(1)	-675(1)	3539(1)	17(1)
C(1)	9335(3)	-2645(2)	3679(2)	31(1)
C(2)	8168(3)	-2518(2)	4313(2)	31(1)
C(3)	7671(3)	-1410(2)	4793(1)	30(1)
C(4)	8423(3)	-498(2)	4662(2)	32(1)
C(5)	9608(3)	-629(2)	4007(2)	33(1)
C(6)	10037(3)	-1679(2)	3506(2)	31(1)
C(7)	7120(3)	2484(2)	3971(1)	19(1)
C(8)	6237(3)	2677(2)	4724(1)	28(1)
C(9)	6515(3)	3401(3)	5285(2)	35(1)
C(10)	7675(3)	3920(2)	5106(2)	35(1)
C(11)	8574(3)	3708(2)	4371(2)	33(1)
C(12)	8296(3)	3000(2)	3804(2)	25(1)
C(13)	4734(2)	2402(2)	3142(1)	17(1)
C(14)	3896(2)	2081(2)	2599(1)	19(1)
C(15)	2178(3)	2655(2)	2714(2)	29(1)
C(16)	3878(2)	1009(2)	1374(1)	18(1)
C(17)	3170(3)	2005(2)	847(1)	24(1)
C(18)	2591(3)	1735(2)	192(2)	27(1)
C(19)	2760(3)	478(2)	48(1)	25(1)
C(20)	3479(3)	-510(2)	572(1)	25(1)
C(21)	4032(3)	-252(2)	1240(1)	22(1)
C(22)	7233(2)	2378(2)	2277(1)	16(1)
C(23)	8403(2)	1997(2)	1695(1)	18(1)
C(24)	9801(3)	811(2)	1784(1)	22(1)
C(25)	8440(2)	2710(2)	897(1)	18(1)
C(26)	8783(3)	2028(2)	186(1)	23(1)
C(27)	8840(3)	2627(2)	-572(1)	28(1)
C(28)	8608(3)	3934(3)	-646(2)	32(1)
C(29)	8318(3)	4609(2)	46(2)	28(1)

C(30)	8199(3)	4032(2)	819(1)	20(1)
C(31)	7881(3)	4830(2)	1545(1)	23(1)
C(32)	5308(3)	6108(2)	1247(2)	34(1)
C(33)	6114(3)	6171(2)	2552(2)	36(1)
Cl(1)	4917(1)	-552(1)	3703(1)	26(1)
Cl(2)	7646(1)	-1053(1)	2128(1)	21(1)
Cl(3)	2799(1)	5482(1)	2731(1)	29(1)
N(1)	4560(2)	1240(2)	2029(1)	19(1)
N(2)	6226(2)	5325(2)	1883(1)	23(1)
P(1)	6764(1)	1555(1)	3212(1)	15(1)

Table A-15.1 Crystal Data and Structure Refinement for 34.

Empirical formula	C ₃₅ H ₄₀ Cl ₅ N ₂ P Pd Ru
Formula weight	904.38
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 10.9956(6) Å α = 90°. b = 15.9017(9) Å β = 96.890(2)°. c = 21.1097(12) Å γ = 90°.
Volume	3664.3(4) Å ³
Z	4
Density (calculated)	1.639 Mg/m ³
Absorption coefficient	1.339 mm ⁻¹
F(000)	1816
Crystal size	0.34 x 0.30 x 0.28 mm ³
Theta range for data collection	2.33 to 26.00°.
Index ranges	-13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -26 ≤ l ≤ 25
Reflections collected	47301
Independent reflections	7194 [R(int) = 0.0446]
Completeness to theta = 26.00°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7056 and 0.6588
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7194 / 0 / 410
Goodness-of-fit on F ²	1.124
Final R indices [I > 2σ(I)]	R1 = 0.0630, wR2 = 0.1690
R indices (all data)	R1 = 0.0712, wR2 = 0.1787
Largest diff. peak and hole	5.232 and -1.660 e.Å ⁻³

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad wR2 = \sqrt{\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}}, \quad w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP.$$

Table A-15.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 34. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	9492(1)	7858(1)	3491(1)	20(1)
Ru(1)	6263(1)	6629(1)	4755(1)	21(1)
C(1)	5781(7)	6958(5)	5687(4)	34(2)
C(2)	5090(7)	6211(5)	5502(4)	37(2)
C(3)	4359(7)	6189(5)	4918(4)	36(2)
C(4)	4315(7)	6911(6)	4505(4)	38(2)
C(5)	4924(7)	7650(5)	4712(4)	35(2)
C(6)	5648(7)	7680(5)	5307(4)	35(2)
C(7)	7837(6)	8469(4)	4624(3)	23(1)
C(8)	8477(8)	8564(5)	5226(4)	37(2)
C(9)	8537(9)	9349(6)	5521(5)	51(2)
C(10)	7974(11)	10027(6)	5222(5)	59(3)
C(11)	7316(10)	9940(5)	4619(5)	51(2)
C(12)	7257(7)	9159(4)	4320(4)	33(2)
C(13)	9310(6)	7132(4)	4315(3)	22(1)
C(14)	9765(6)	6329(4)	4153(3)	24(1)
C(15)	11082(7)	6153(5)	4329(4)	34(2)
C(16)	9452(7)	4954(4)	3617(4)	32(2)
C(17)	9743(7)	5021(5)	2938(4)	34(2)
C(18)	9228(8)	5632(6)	2520(4)	45(2)
C(19)	9485(10)	5683(7)	1901(5)	62(3)
C(20)	10292(10)	5106(9)	1690(6)	70(3)
C(21)	10838(10)	4519(7)	2097(5)	60(3)
C(22)	10561(8)	4464(6)	2721(5)	50(2)
C(23)	7697(6)	7614(4)	3418(3)	21(1)
C(24)	6806(6)	7513(4)	2939(3)	22(1)
C(25)	5487(6)	7363(5)	3035(4)	34(2)
C(26)	7019(6)	7527(4)	2251(3)	23(1)
C(27)	6504(7)	6894(5)	1842(4)	32(2)
C(28)	6650(8)	6876(5)	1200(4)	41(2)
C(29)	7283(7)	7524(6)	946(4)	39(2)

C(30)	7773(7)	8161(5)	1332(3)	34(2)
C(31)	7653(6)	8175(4)	1987(3)	26(1)
C(32)	8171(6)	8905(4)	2377(3)	25(1)
C(33)	10288(7)	8564(5)	2281(3)	30(2)
C(34)	9782(7)	9577(4)	3054(4)	33(2)
C(35)	7705(9)	3475(7)	7375(5)	60(3)
Cl(1)	8019(2)	5955(1)	5312(1)	38(1)
Cl(2)	6264(2)	5593(1)	3909(1)	28(1)
Cl(3)	11683(2)	8085(1)	3748(1)	32(1)
Cl(4)	6784(2)	4254(2)	6984(1)	61(1)
Cl(5)	7227(3)	3191(3)	8109(2)	95(1)
N(1)	9419(5)	8766(3)	2736(3)	23(1)
N(2)	9046(5)	5747(3)	3868(3)	26(1)
P(1)	7697(1)	7427(1)	4259(1)	19(1)

Table A-16.1 Crystal Data and Structure Refinement for 36.

Empirical formula	C ₃₂ H ₄₂ Cl ₅ N ₂ P Pd Ru	
Formula weight	870.37	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 10.5582(3) Å	α = 90°.
	b = 25.0048(7) Å	β = 90.197(2)°.
	c = 13.8966(4) Å	γ = 90°.
Volume	3668.76(18) Å ³	
Z	4	
Density (calculated)	1.576 Mg/m ³	
Absorption coefficient	1.334 mm ⁻¹	
F(000)	1752	
Crystal size	0.40 x 0.40 x 0.30 mm ³	
Theta range for data collection	1.63 to 33.25°.	
Index ranges	-16 ≤ h ≤ 16, -38 ≤ k ≤ 38, -21 ≤ l ≤ 21	
Reflections collected	89447	
Independent reflections	13989 [R(int) = 0.0762]	
Completeness to theta = 33.25°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6904 and 0.6175	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	13989 / 77 / 415	
Goodness-of-fit on F ²	1.117	
Final R indices [I > 2σ(I)]	R1 = 0.0610, wR2 = 0.1879	
R indices (all data)	R1 = 0.0835, wR2 = 0.2298	
Largest diff. peak and hole	3.085 and -1.559 e.Å ⁻³	

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad wR2 = \sqrt{\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}}, \quad w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP.$$

Table A-16.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 36. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	584(1)	1550(1)	3235(1)	24(1)
Ru(1)	4145(1)	458(1)	1760(1)	21(1)
C(1)	6114(4)	621(2)	2108(4)	35(1)
C(2)	6145(5)	264(3)	1317(4)	43(1)
C(3)	5484(5)	-209(2)	1335(4)	48(1)
C(4)	4771(5)	-338(2)	2174(5)	47(1)
C(5)	4806(5)	-12(2)	2996(4)	37(1)
C(6)	5485(4)	470(2)	2965(3)	34(1)
C(7)	2315(4)	539(2)	3756(3)	25(1)
C(8)	1681(5)	50(2)	3750(4)	37(1)
C(9)	1564(6)	-232(2)	4606(5)	54(2)
C(10)	2119(7)	-50(3)	5443(5)	63(2)
C(11)	2741(7)	431(3)	5461(4)	56(2)
C(12)	2854(5)	723(2)	4611(3)	36(1)
C(13)	2452(4)	1589(2)	3028(3)	23(1)
C(14)	3304(4)	1985(2)	3025(3)	24(1)
C(15)	4700(4)	1904(2)	2799(4)	35(1)
C(16)	2950(4)	2546(2)	3252(3)	28(1)
C(17)	3387(5)	2949(2)	2632(5)	44(1)
C(18)	3137(7)	3487(2)	2828(6)	55(2)
C(19)	2465(6)	3625(2)	3620(7)	62(2)
C(20)	2033(5)	3232(2)	4245(5)	46(1)
C(21)	2249(4)	2685(2)	4075(4)	34(1)
C(22)	1780(5)	2281(2)	4768(4)	40(1)
C(23)	-448(6)	2459(3)	4470(6)	60(2)
C(24)	202(7)	1657(3)	5285(4)	55(2)
C(25)	912(3)	939(2)	2218(3)	23(1)
C(26)	493(4)	1142(2)	1318(3)	26(1)
C(27)	-847(5)	1036(3)	1042(4)	44(1)
C(28)	877(6)	1652(3)	-193(4)	48(1)
C(29)	1373(6)	1353(3)	-1093(4)	52(1)

C(30)	860(7)	792(3)	-1214(4)	54(2)
C(31)	1226(8)	553(4)	-2179(5)	68(2)
C(32)	4630(20)	1814(9)	6248(16)	138(6)
Cl(4)	4250(16)	2423(5)	6619(8)	333(8)
Cl(5)	5904(12)	1736(6)	5503(8)	226(5)
C(32A)	5360(20)	1737(17)	6442(19)	120(9)
Cl(4A)	6093(16)	1309(7)	5597(12)	158(6)
Cl(5A)	3941(11)	1484(3)	6865(8)	108(4)
Cl(1)	4154(1)	1204(1)	645(1)	30(1)
Cl(2)	2378(1)	70(1)	907(1)	26(1)
Cl(3)	-1663(1)	1392(1)	3356(1)	45(1)
N(1)	1238(4)	1395(2)	704(3)	34(1)
N(2)	524(4)	2038(2)	4511(3)	39(1)
P(1)	2552(1)	902(1)	2635(1)	19(1)

Table A-17.1 Crystal Data and Structure Refinement for (R_PS_CS_C)-37.

Empirical formula	C ₃₂ H ₄₃ Cl ₃ N ₂ O _{0.50} P Pd Ru
Formula weight	808.47
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P2(1)2(1)2
Unit cell dimensions	a = 14.7818(6) Å α = 90°. b = 21.3958(8) Å β = 90°. c = 10.6629(4) Å γ = 90°.
Volume	3372.3(2) Å ³
Z	4
Density (calculated)	1.592 Mg/m ³
Absorption coefficient	1.292 mm ⁻¹
F(000)	1636
Crystal size	0.40 x 0.08 x 0.04 mm ³
Theta range for data collection	2.36 to 26.59°.
Index ranges	-18 ≤ h ≤ 18, -25 ≤ k ≤ 26, -13 ≤ l ≤ 13
Reflections collected	30469
Independent reflections	6981 [R(int) = 0.0383]
Completeness to theta = 26.59°	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9501 and 0.6260
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6981 / 475 / 473
Goodness-of-fit on F ²	1.093
Final R indices [I > 2σ(I)]	R1 = 0.0243, wR2 = 0.0537
R indices (all data)	R1 = 0.0298, wR2 = 0.0564
Absolute structure parameter	-0.04(2)
Largest diff. peak and hole	0.361 and -0.417 e.Å ⁻³

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad wR2 = \sqrt{\{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}}, \quad w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP.$$

Table A-17.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ($R_P S_C S_C$)-37. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(16)	500(40)	7307(14)	10457(13)	57(7)
C(17)	370(30)	6601(14)	10570(30)	73(5)
C(18)	850(30)	6164(14)	9690(40)	77(7)
C(19)	190(40)	5614(19)	9620(50)	127(13)
C(16A)	251(5)	7336(3)	10435(4)	42(2)
C(17A)	1031(4)	6932(3)	10952(5)	71(2)
C(18A)	1213(5)	6342(3)	10306(8)	88(2)
C(19A)	451(7)	5879(4)	10382(9)	122(3)
C(1)	3141(8)	9373(9)	7590(20)	41(4)
C(2)	2814(13)	9258(8)	6375(17)	34(4)
C(3)	1979(14)	9521(9)	5994(12)	35(4)
C(4)	1472(12)	9887(7)	6820(20)	36(4)
C(5)	1810(15)	10016(6)	8015(18)	38(4)
C(6)	2643(15)	9768(8)	8408(13)	37(4)
C(1A)	3180(5)	9258(5)	7165(13)	35(2)
C(2A)	2610(8)	9287(5)	6126(9)	31(2)
C(3A)	1803(8)	9654(6)	6169(9)	33(2)
C(4A)	1596(7)	9977(4)	7267(13)	34(3)
C(5A)	2192(10)	9967(4)	8297(10)	40(3)
C(6A)	2978(8)	9608(6)	8247(10)	39(3)
Pd(1)	671(1)	6863(1)	6313(1)	20(1)
Ru(1)	1792(1)	8991(1)	7715(1)	24(1)
C(7)	1126(2)	8298(1)	4949(3)	21(1)
C(8)	1770(2)	8152(2)	4045(3)	28(1)
C(9)	1663(2)	8354(2)	2827(3)	34(1)
C(10)	915(3)	8704(2)	2497(3)	37(1)
C(11)	278(2)	8865(2)	3387(3)	34(1)
C(12)	382(2)	8665(2)	4612(3)	29(1)
C(13)	220(2)	7732(1)	6970(3)	23(1)
C(14)	-77(2)	7576(1)	8203(3)	28(1)
C(15)	-1070(2)	7494(2)	8413(4)	44(1)

C(20)	1822(2)	7333(1)	6610(2)	18(1)
C(21)	2665(2)	7174(1)	6921(2)	19(1)
C(22)	3456(2)	7629(1)	6920(3)	28(1)
C(23)	2910(2)	6525(1)	7330(3)	19(1)
C(24)	3360(2)	6483(2)	8480(3)	27(1)
C(25)	3618(2)	5914(2)	8981(3)	34(1)
C(26)	3429(2)	5372(2)	8346(3)	31(1)
C(27)	2989(2)	5404(1)	7212(3)	30(1)
C(28)	2718(2)	5974(1)	6683(3)	22(1)
C(29)	2245(2)	5954(2)	5416(3)	29(1)
C(30)	2642(3)	6403(2)	4438(3)	38(1)
C(31)	920(3)	5503(2)	6399(5)	51(1)
C(32)	826(3)	5904(2)	4293(4)	63(1)
Cl(1)	295(1)	9019(1)	8583(1)	46(1)
Cl(2)	2269(1)	8309(1)	9409(1)	37(1)
Cl(3)	-857(1)	6471(1)	6017(1)	41(1)
N(1)	481(2)	7515(1)	9136(2)	30(1)
N(2)	1236(2)	6011(1)	5552(3)	33(1)
O(1)	8485(5)	5751(3)	8716(8)	83(2)
P(1)	1303(1)	8094(1)	6595(1)	18(1)

Table A-18.1 Crystal Data and Structure Refinement for 42.

Empirical formula	C ₃₇ H ₄₄ Cl ₉ N ₂ P Pd Ru	
Formula weight	1074.23	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.1958(10) Å	α = 111.385(6)°.
	b = 14.1155(14) Å	β = 91.044(7)°.
	c = 17.0530(17) Å	γ = 105.238(7)°.
Volume	2187.1(4) Å ³	
Z	2	
Density (calculated)	1.631 Mg/m ³	
Absorption coefficient	1.372 mm ⁻¹	
F(000)	1076	
Crystal size	0.40 x 0.20 x 0.10 mm ³	
Theta range for data collection	1.29 to 29.00°.	
Index ranges	-13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -23 ≤ l ≤ 23	
Reflections collected	33322	
Independent reflections	11519 [R(int) = 0.0601]	
Completeness to theta = 29.00°	99.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8750 and 0.6098	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	11519 / 40 / 465	
Goodness-of-fit on F ²	1.087	
Final R indices [I > 2σ(I)]	R1 = 0.0625, wR2 = 0.1757	
R indices (all data)	R1 = 0.1014, wR2 = 0.2127	
Largest diff. peak and hole	2.153 and -1.387 e.Å ⁻³	

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad wR2 = \sqrt{\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}}, \quad w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP.$$

Table A-18.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 42. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	5533(1)	2217(1)	2593(1)	22(1)
Ru(1)	7947(1)	4715(1)	1218(1)	22(1)
C(1)	7069(9)	4923(6)	143(5)	39(2)
C(2)	8436(9)	5491(7)	265(6)	43(2)
C(3)	9069(9)	6244(6)	1065(6)	45(2)
C(4)	8269(10)	6422(6)	1752(5)	46(2)
C(5)	6849(9)	5903(6)	1609(5)	39(2)
C(6)	6249(8)	5159(6)	802(5)	37(2)
C(7)	4739(6)	3362(5)	1424(4)	23(1)
C(8)	4224(7)	2719(5)	584(4)	28(1)
C(9)	2870(8)	2558(6)	278(5)	38(2)
C(10)	2046(8)	3049(7)	801(6)	41(2)
C(11)	2551(8)	3714(7)	1634(6)	42(2)
C(12)	3905(7)	3880(6)	1953(5)	33(2)
C(13)	6429(6)	3774(5)	2909(4)	23(1)
C(14)	6962(7)	4615(5)	3649(4)	25(1)
C(15)	7622(8)	5725(5)	3668(5)	34(2)
C(16)	6995(7)	4514(5)	4487(4)	27(1)
C(17)	8220(8)	5002(6)	5041(5)	36(2)
C(18)	8319(9)	4937(7)	5831(5)	42(2)
C(19)	7216(11)	4372(8)	6077(5)	51(2)
C(20)	5983(9)	3892(7)	5539(5)	39(2)
C(21)	5842(8)	3948(5)	4745(4)	29(1)
C(22)	4476(7)	3462(6)	4209(5)	32(1)
C(23)	2820(8)	1994(7)	3139(6)	48(2)
C(24)	4320(11)	1629(7)	4008(6)	52(2)
C(25)	6561(6)	2252(5)	1532(4)	21(1)
C(26)	7698(6)	1902(5)	1680(4)	22(1)
C(27)	8827(7)	2542(5)	2404(5)	31(1)
C(28)	6823(8)	304(6)	383(4)	33(2)
C(29)	8675(7)	437(5)	1402(4)	27(1)

C(30)	8215(9)	-151(7)	1898(6)	46(2)
C(31)	9011(11)	-712(8)	2076(7)	61(3)
C(32)	10244(10)	-703(7)	1774(6)	53(2)
C(33)	10696(9)	-118(8)	1293(6)	53(2)
C(34)	9907(8)	461(7)	1108(5)	38(2)
C(35)	3545(8)	7806(7)	1776(8)	63(3)
C(36)	6252(14)	9148(13)	3653(12)	209(14)
C(37)	1400(20)	8838(12)	4815(8)	165(7)
Cl(8)	1164(14)	7772(8)	5117(9)	357(9)
Cl(9)	820(20)	8628(12)	3801(7)	390(9)
Cl(1)	4597(2)	303(1)	1978(1)	44(1)
Cl(2)	8354(2)	3088(1)	274(1)	32(1)
Cl(3)	9840(2)	4932(1)	2194(1)	34(1)
Cl(4)	5171(3)	7626(3)	1588(2)	80(1)
Cl(5)	2516(4)	6825(3)	2080(2)	90(1)
Cl(6)	4735(10)	9056(8)	4113(5)	319(8)
Cl(7)	7063(10)	8229(8)	3728(5)	220(4)
N(1)	4230(6)	2353(5)	3580(4)	33(1)
N(2)	7780(5)	959(4)	1172(3)	23(1)
P(1)	6539(2)	3626(1)	1822(1)	19(1)