Developing a new phosphorus-carbon bond synthesis

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**DEVELOPING A NEW
PHOSPHORUS-CARBON BOND SYNTHESIS**

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Abstract

This thesis is about developing a new phosphorus-carbon bond synthesis based on electrophilic terminal phosphinidene chemistry and finding application for this methodology. The first chapter gives a brief account of the general methods in forming phosphorus-carbon bonds. The second chapter details the works of the author on using the reaction of electrophilic terminal phosphinidene complexes with arylboronic acids in presence of potassium phosphate to form phosphorus-carbon bond. Preliminary mechanistic study was carried out, and the results tentatively suggest that the reaction proceeds via the insertion of phosphinidene complex into the boron-oxygen bond of arylboronic acid, followed by a 1,2-migration of the aryl group onto the phosphorus atom. The third chapter is based on exploring and expanding the scope and application for this new P-C bond. It was found out that the reaction pathway of terminal phosphinidene complexes and alkenylboronic acids can be altered by potassium phosphate. In the absence of phosphate, [1+2] cycloaddition proceeds to give phosphirane complexes; P-C bond formation proceeds in the presence of phosphate to give secondary alkenylphosphine complexes. Computations were made to understand this shift in reaction. Attempts to synthesise other organophosphorus compounds were also made.

List of publications

1. "Using Monovalent Phosphorus Compounds to Form P-C Bonds." Ng, Yong Xiang; Mathey, Francois, *Angewandte Chemie-International Edition*, **2013**, 52, 14140-14142.
2. "Mechanism of Phosphinidene Complex Arylation by Arylboronic Acids." Ng, Yong Xiang; Mathey, Francois, *Organometallics*, **2014**, 33, 1322-1324.
3. "The Reaction of Terminal Phosphinidene Complexes [RP-W(CO)₅] with Vinylboronic Acids: Cycloaddition vs P-C bond Formation." Ng, Yong Xiang; Mathey, Francois, *European Journal of Inorganic Chemistry*, **2016**, 616-619.

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Abbreviations and Symbols

δ	NMR shift in ppm
$^{\circ}$	degrees
$^{\circ}\text{C}$	degree celsius
$\text{\AA}$	angstroms
Σ	summation
acac	acetylacetonate
Ad	adamantyl
AIBN	azobisisobutyronitrile
Ar	aryl
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
Bn	benzyl
br	broad
Bz	benzoyl
calcd	calculated
cat	catalyst
cod	1,5-cyclooctadiene
Cp	cyclopentadiene
Cp*	1,2,3,4,5-pentamethylcyclopentadiene
Cy	cyclohexyl
d	doublet
DABCO	1,4-diazabicyclo[2.2.2]octane

DBN	1,5-diazabicyclo[4.3.0]non-5-ene
DCM	dichloromethane
dcype	1,2-bis(dicyclohexylphosphino)ethane
dd	doublet of doublets
ddd	doublet of doublets of doublets
Deg	degrees
DFT	density functional theory
DMA	dimethylacetamide
DMAD	dimethyl acetylenedicarboxylate
DMF	dimethylformamide
Dmp	2,6-dimesitylphenyl
DMPU	1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone
DMSO	dimethyl sulfoxide
dppe	1,2-bis(diphenylphosphino)ethane
dppf	1,1'-bis(diphenylphosphino)ferrocene
dppp	1,3-bis(diphenylphosphino)propane
dr	diastereomeric ratio
ee	enantiomeric excess
eq.	equivalent
et al.	et alia
Fc	ferrocenyl
Fu	furyl

h	hour
HOMO	highest occupied molecular orbital
HRMS	high resolution mass spectroscopy
h ν	light
Hz	hertz
<i>i</i> -Pr	isopropyl
iPr-PHOX	2-[2-(diphenylphosphino)phenyl]-4-isopropyl-4,5-dihydrooxazole
Is*	2,4,6-triisopropylphenyl
<i>J</i>	coupling constant
kcalmol ⁻¹	kilocalorie per mole
LDA	lithium diisopropylamide
LUMO	lowest unoccupied molecular orbital
m	multiplet
Mes	mesitylene
Mes*	2,4,6-tri(<i>tert</i> -butyl)phenyl
mol.	mole
mol%	mole percent
MS	molecular sieve
m/z	mass-to-charge ratio
<i>n</i> -Bu	normal butyl
NMO	<i>N</i> -methylmorpholine- <i>N</i> -oxide
NMP	<i>N</i> -methyl-2-pyrrolidone

NMR	nuclear magnetic resonance
OAc	acetate
<i>p</i>	para
Ph	phenyl
ppm	parts per million
Py	pyridine
PyBroP	bromotripyrrolidinophosphonium hexafluorophosphate
q	quartet
rt	room temperature
t	triplet
TBHP	<i>tert</i> -butyl hydroperoxide
<i>t</i> -Bu	<i>tert</i> -butyl
TEA	triethylamine
TfO	trifluoromethanesulfonate
Th	thienyl
THF	tetrahydrofuran
TMS	trimethylsilyl
<i>t</i> -Pent	<i>tert</i> -pentyl
Ts	tosyl
V-40	1,1'-azobis(cyclohexane-1-carbonitrile)

Chapter 1

Introduction to Phosphorus-Carbon Bond Synthesis

The origin of organophosphorus chemistry can be traced back to 1855 with Hofmann's work on trialkylphosphines.^[1] Since then, many discoveries were made and the field of organophosphorus chemistry has grown enormously.^[2-6] Organophosphorus compounds are interesting and useful chemicals in catalysis,^[7-16] material sciences,^[17-18] organic synthesis,^[19-21] and biological chemistry.^[22-25] These compounds can be easily characterised by general stereoscopic methods, particularly phosphorus (³¹P) NMR.^[26]

In this chapter, an overview of the synthesis of phosphorus-carbon single bonds in discrete molecules will be presented in the following sections: P-C bond synthesis via nucleophilic reactions, hydrophosphination and related reactions, transition metal-catalysed P-C bond syntheses, cycloadditions, ionic and radical P-C bond formations, and other forms of P-C bond formations. P-C bond formations in the syntheses of organophosphorus polymers will not be discussed in this chapter.^[27-29]

1.1 P-C bond formation via nucleophilic reactions

Nucleophilic substitution is the most widely used method in forming P-C bonds. This section is presented into two parts: nucleophilic substitutions on electrophilic phosphorus centres and nucleophilic attacks by phosphorus nucleophiles.

1.1.1 Nucleophilic substitutions on electrophilic phosphorus centres.

This route involves simple nucleophilic substitutions by carbanions onto electrophilic phosphorus centres. It is the most popular route in phosphine syntheses due to the wide variety of organoalkali reagents and organophosphorus halides available and generally high yields.^[2, 14, 16, 30-35]

C-chiral phosphines can be formed via simple nucleophilic substitutions on halophosphines. P-chiral phosphorus compounds can be prepared via similar routes with chiral phosphinates, phosphinic halides, halophosphanylboranes.^[36-39] In general, reactions involving alkynyl/aryllithium and magnesium reagents invert the stereo-configuration on phosphorus centre, while those involving alkyl lithium and magnesium reagents retain the P-chirality (Scheme 1.1). The retention of P-chirality could be due to the metal-halogen exchange followed by the reaction of the phosphoranyl anion with the resulting alkyl halides.

Scheme 1.1 Stereo-inversion and retention of P-centre based on different types of carbon nucleophiles.

Besides forming phosphines, organolithium and Grignard reagents are also used in the syntheses of phosphorus heterocycles.^[4, 17] The first phosphorus-carbon ring (Scheme 1.2) and the first phosphole (Scheme 1.3) were synthesised via reaction of dichlorophenylphosphine with organoalkali metal reagents.^[40-41]

Scheme 1.2 Synthesis of first phosphorus-carbon ring 1-phenylphosphinane.

Scheme 1.3 Synthesis of first phosphole.

This method has been expanded to synthesise a variety of P-heterocycles such as the ladder-type P,S-bridged trans-stilbenes (Scheme 1.4).^[42]

Scheme 1.4 Synthesis of ladder-type P,S-bridged trans-stilbenes.

These P-C bond syntheses using organoalkali reagents are useful as a wide range of organoalkali metal reagents and halophosphines can be utilised and the yields are generally high. However, this method does not tolerate functional groups such as carbonyls.

Various organometallacycles are also used in the formations of phosphorus heterocycles. P-heterocycles can be formed via zirconium-phosphorus exchanges between dichlorophosphines with zirconium metallacycles.^[43-46] The Fagan-Nugent method is a versatile phosphole synthesis due to the wide variety of symmetric and asymmetric zirconacyclopentadienes available and generally gives high yields (Scheme 1.5).^[43] Like

the organoalkali metal reagents, reactive groups, such as carbonyls, are not compatible with zirconium metallacycles.

Scheme 1.5 Synthesis of phospholes via Fagan-Nugent method.

Titanium metallacycles are used in the synthesis of phospholes via the Urabe-Sato reagent (Scheme 1.6).^[47-49] This method is a better phosphole synthesis due to its high functional group tolerance. Like its asymmetric counterpart used in the Fagan-Nugent method, a link group is requested for regiocontrol.

Scheme 1.6 Synthesis of phosphole using Urabe-Sato reagent.

Phosphirenes, phosphetes and phosphetane can also be formed via titanium metallacycles.^[50-54] However, this method is not commonly used as other methods such as cycloadditions are more convenient and have wider substrate scopes.

Another example of P-C bond formation via metallacycle is the reaction of 1,4-dihydro-1,1-dibutylstannabenzene with phosphorus tribromide to give a dihydrophosphinine which is converted into the parent phosphinine (Scheme 1.7).^[55]

Scheme 1.7 Synthesis of parent phosphinine via stannacycle.

P-C bond is also formed when organoalkali metal reagents are added to elemental phosphorus P_4 . However these reactions are typically complicated and the yields are generally low.^[56-57] Recently, Lammertsma reported a way to stabilise the bicyclo[1.1.0]tetraphosphabutane anion, formed via the reaction of bulky organolithium with P_4 , with Lewis acid (Scheme 1.8).^[58] They were able to further form a second P-C bond by methylating the phosphide.

Scheme 1.8 Functionalisation of P_4 .

1.1.2 Nucleophilic substitutions by phosphorus nucleophiles

Phosphenides, like carbanions, are widely used in P-C bond formation via nucleophilic substitutions on carbon electrophiles. Phosphenides can be generated from phosphines via deprotonation and from halophosphines via metal-halogen exchange. The synthesis of the first phosphirane by Wagner in 1963 was achieved via the reaction of sodium phosphenide with 1,2-dichloroethane in ammonia.^[59] The phosphenide method has since

been used to synthesise other phosphiranes and even phosphetanes due to its simple operation.^[60-63] Phospholides are generally formed via cleavage of P-Ph bonds in phenylphospholes by alkaline metals and via deprotonations of 2*H*-phospholes.^[4, 64] Phospholides can also be obtained by treatment of the open-chain acetylenic phosphines with an excess of lithium (Scheme 1.9).^[65]

Scheme 1.9 Synthesis of phospholides via lithiation.

Functional groups can be introduced onto the phosphorus centres of phospholes via phospholides, and subsequently onto the α -position of the phosphole ring via [1,5] sigmatropic shifts (Scheme 1.10).^[4, 66]

Scheme 1.10 Nucleophilic substitutions of carbon electrophiles by phospholide.

P-chiral tertiary phosphine-borane complexes can be formed via secondary phosphinide-borane complexes. Secondary phosphinide-borane complexes are generally formed from secondary phosphine-boranes via deprotonation (Scheme 1.11),^[37, 67-69] and from chlorophosphine-borane via metal-halogen exchange with *tert*-butyllithium (Scheme 1.12).^[36] Stereo-configuration of phosphorus centre is always retained. This P-C bond synthesis has been extended to form a series of enantiopure P-chiral bidentate ligands.

Scheme 1.11 Synthesis of tertiary phosphine borane via deprotonation.

Scheme 1.12 Synthesis of tertiary phosphine borane via metal-halogen exchange.

The advantages of using phosphinide to form P-C bond are that yields are generally high and P-chiral phosphorus species can be formed. However, the phosphinide species must not contain reactive groups such as carbonyls.

Transient phosphinidenoid tungsten complex **1** reported by Streubel is also used in the synthesis of organophosphorus compounds such as oxaphosphirane and 1,2-oxaphosphetane complexes which are difficult to synthesise (Scheme 1.13).^[70-74]

Scheme 1.13 Reactions of phosphinidenoid tungsten complex **1** with various trapping reagents.

McKee and Lammertsma investigated the mechanism of CuCl-catalysed generation of phosphinidene complex from 7-phosphanorbornadiene complex and the subsequent addition to alkenes.^[75] They discovered that the reactive intermediate is a phosphinidenoid complex $[\text{W}(\text{CO})_5(\text{PR}(\text{Cu-L})\text{Cl})]$ (Scheme 1.14).

Scheme 1.14 CuCl-catalysed reaction of 7-phosphanorbornadiene with alkene featuring a Cu-phosphinidenoid complex.

A recent report by Mathey on the reaction of 7-phosphanorbornadiene and boron trichloride also features a phosphinidenoid intermediate (Scheme 1.15).^[76]

Scheme 1.15 Reaction of 7-phosphanorbornadiene with boron trichloride.

Michaelis-Arbuzov reaction is a common method used in the synthesis of organophosphorus compounds containing $\text{P}=\text{O}$ group.^[30, 77] The original reaction involves the reaction of phosphite with alkyl halide to form phosphonate, a conversion of a P(III) compound to a P(V) compound (Scheme 1.16).

Scheme 1.16 Michaelis-Arbuzov reaction.

It is a common method in phosphonate formation for use in the Horner–Wadsworth–Emmons reaction.^[78] There are a few limitations to the Arbuzov reaction. Arylhalides cannot be utilised in the reaction and the alkoxyl groups on the starting phosphorus species must be the same to avoid mixture of products. Many variations of the Arbuzov reaction have been developed, such as the Michaelis-Becker reaction, Abramov reaction, Pudovik reaction and Kabachnik-Fields reaction (Scheme 1.17).^[30, 79-80]

Scheme 1.17 Arbuzov-related reactions.

Arbuzov rearrangements of phosphites, phosphonites and phosphinites catalysed by trimethylsilane triflate,^[81] trimethylsilane halides,^[82-83] and ionic liquids were also reported.^[84-85] N-heterocyclic-catalysed Abramov reaction was also reported.^[86] A recent paper on *n*-butyllithium catalysed Pudovik reaction of aldehydes and unactivated ketones

to form α -hydroxyphosphonates was published (Scheme 1.18).^[87] This improved method is a simple and efficient access to α -hydroxyphosphonates which are an intriguing class of compounds in biological and pharmaceutical studies.

Scheme 1.18 *n*-Butyllithium catalysed Pudovik reaction of aldehydes and unactivated ketones.

An efficient one-pot synthesis of α -acyloxyphosphine oxides from aldehydes and secondary phosphine oxides mediated by lithium *tert*-butoxide was also reported recently (Scheme 1.19).^[88] The authors proposed that the α -hydroxyphosphine oxide formed from the initial Pudovik reaction reacts with aldehyde, then followed by either a 1,2 or 1,3 proton shift and protonation to form the isolated product. A variety of α -acyloxyphosphine oxides can be synthesised easily via this method.

Scheme 1.19 Base-mediated one-pot synthesis of α -acyloxyphosphine oxides.

In general, Arbuzov and related reactions are simple and straightforward accesses to P=O containing organophosphorus compounds with good to excellent yields. Stereoselectivity is usually not considered.

Nucleophilic reactions between tertiary phosphines and alkyl halides form phosphonium salts. The most widely known phosphonium salts are those of the triphenylphosphonium halides which are converted into phosphonium ylides in Wittig reaction (Scheme 1.20).^[21, 89-90]

Scheme 1.20 Generation of triphenylphosphonium halide and subsequent Wittig reaction.

Beside alkyl halides, neutral trivalent phosphorus compounds can also perform nucleophilic attacks on carbon-carbon and carbon-heteroatom multiple bonds. Phosphamichael addition is a common method in forming P-C bonds using various Michael acceptors and Baylis-Hillman adducts.^[91-93] Generally, the yields are high and chirality can also be introduced. A series of bidentate diphosphines can also be formed in good yields via the addition of symmetric and asymmetric P-P diphosphines to Michael acceptors and via the condensation of silylphosphine with chloro-organic species (Scheme 1.21).^[94-97]

Scheme 1.21 General synthesis of bidentate diphosphines via P-P and P-Si phosphines.

Cross-dehydrogenative coupling (CDC) is a versatile and atom-economy efficient C-C bond formation method,^[98-100] and it has been expanded to P-C bond formation recently.^[100-108] Currently for the non-metal catalysed P-C bond forming CDC, the carbon substrate is limited to N-aryl tetrahydroisoquinoline and quinoline N-oxide, and the phosphorus species used are H-phosphonates and secondary phosphines.^[100-106] The CDC proceeds via nucleophilic attack of the phosphorus unit onto the iminium ion, generated from SET and proton loss, and the subsequent proton loss gives the phosphonate or phosphine oxide (Scheme 1.22).

Scheme 1.22 CDC of tetrahydroisoquinoline with H-phosphonates and secondary phosphines.

Similarly, the CDC of quinoline N-oxide proceeds via a nucleophilic attack by the phosphorus unit onto the iminium followed by loss of water (Scheme 1.23).

Scheme 1.23 CDC of quinoline N-oxide with H-phosphonates.

P-arylation is another method of synthesising arylphosphoryl compounds. The reaction proceeds via the nucleophilic attack of alkoxyphosphines onto the benzyne, which is

generated in-situ from the reaction of silylaryl triflates and fluoride, followed by protonation and an Arbuzov-like rearrangement to give the final product as a phosphoryl compound (Scheme 1.24).^[109-110] The yields of these reactions are high and the reactions proceed at ambient temperature. The *ortho*-position of the aryl ring can be functionalised by introducing carbon dioxide during the reaction.

Scheme 1.24 P-arylation of alkoxy phosphine.

Allylic phosphinites can undergo [2,3] sigmatropic rearrangements to form allylic phosphinates (Scheme 1.25). This method is used to synthesise a series of C-chiral methylenecyclopropylphosphine oxides,^[111-112] and was recently extended to the synthesis of highly enantioenriched diphosphines with stereogenic P and C centres.^[113]

Scheme 1.25 General representation of P-C bond formation via [2,3] sigmatropic rearrangement of allylic phosphinate.

P-heterocycles can also be synthesised via trivalent phosphorus species. The synthesis of the first phosphinine from the reaction of tris(hydroxymethyl)phosphine with 2,4,6-triphenylpyrylium tetrafluoroborate was reported by Markl (Scheme 1.26).^[114] Markl then

expanded his phosphinine synthesis by using different triarylpyryliums and phosphines.^[115-116]

Scheme 1.26 Synthesis of first phosphinine.

Until today, this method is still used as a straightforward synthesis of 2,4,6-triarylphosphinine because of the good yields and a wide variety of triarylpyrylium salts are available.^[117-118]

Polycyclic annulated phosphole derivatives can be synthesised via intramolecular cascade cyclisation (Scheme 1.27).^[119-120]

Scheme 1.27 Synthesis of annulated phosphole derivative via intramolecular cascade cyclisation.

The cyclisation process is initiated by the attack of phosphorus onto the C-C triple bond, and it generally proceeds at ambient conditions and the yields are good.

Overall, the P-C bond synthesis via nucleophilic substitutions is a highly versatile and straightforward method which can be used to synthesis a wide range of phosphines (and derivatives) and P-heterocycles, particularly phospholes and derivatives, in good to excellent yields. P-chiral phosphine derivatives can also be formed from P-chiral starting materials. The main drawback of this method is that not all of the reactions are atom-economy efficient and enantioselective.

1.2 P-C bond formation via the additions of P-H bond onto C-X multiple bonds

The addition of P-H bond onto C-X (X = C, N, O) multiple bonds is a popular area of research due to the reaction's efficient atom economy as a method of synthesising P-C bonds.^[35, 121-125] When asymmetric alkenes and alkynes are involved, regioselectivity and stereoselectivity become an issue of consideration. In the simplest case, the products can either be the Markovnikov or anti-Markovnikov addition products (Scheme 1.28).

Scheme 1.28 Regio- and stereoselectivity issues in hydrophosphination.

The regioselectivity and stereoselectivity are dependent on reactions conditions and mechanistic pathways. The main focus of this section is on the addition of P-H bond onto C-C multiple bonds. Hydrophosphinations of C=O and C=N will be briefly mentioned as these reactions overlap with other reactions such as Pudovik reaction.

1.2.1 Classic additions of P-H bond onto C-X multiple bonds

Hydrophosphination can be carried out by simply heating phosphines and their derivatives with alkenes together.^[35, 126] Microwave-assisted hydrophosphinations were also investigated.^[127] Acid-catalysed hydrophosphinations give the Markovnikov addition products via stabilised carbocations (Scheme 1.29).^[35]

Scheme 1.29 Acid-catalysed hydrophosphination.

Base-catalysed additions of P-H bonds onto C-X multiple bonds were also reported.^[35, 87, 128-129] Anti-Markovnikov addition products are generally obtained. P-heterocycles such as phosphepine can also be synthesised via dihydrophosphination (Scheme 1.30).^[130]

Scheme 1.30 Synthesis of phosphepine complex via KOH-assisted hydrophosphination.

Hydrophosphinations promoted by various radical initiators, such as air and light, were also published.^[35, 131-136] P-chiral phosphinates can be obtained via radical hydrophosphinylation of various alkenes with P-chiral H-phosphinate in high yields (Scheme 1.31).

Scheme 1.31 Synthesis of P-chiral phosphinate via radical hydrophosphinylation.

These hydrophosphinations are easy to be carried out and the yields generally range from moderate to excellent. The downside of these simple reactions is that stereoselectivity is basically absent.

1.2.2 Metal-catalysed additions of P-H bond onto C-X multiple bonds

There are many metal-catalysed hydrophosphinations.^[122-125] This subsection will focus mainly on special and recent examples. There are two possible pathways in the general proposed mechanisms for metal-catalysed hydrophosphination of alkenes and alkynes (Scheme 1.32). The first route is the alkene/alkyne insertion into M-P bond followed by C-H reductive elimination; the second route is the alkene/alkyne insertion into M-H bond followed by C-P reductive elimination. The regio- and stereoselectivity are dependent on the metal catalysts/ligands and reaction conditions.

Scheme 1.32 General proposed mechanisms for metal-catalysed hydrophosphinations of alkenes (A) and alkynes (B).

Mechanism studies reveal that P-M insertions generally occur in Pd- and Pt-catalysed hydrophosphinations, while M-H insertion generally occurs in Rh-catalysed hydrophosphination.^[137-140]

Rare earth metals are used in several hydrophosphinations.^[141-143] Intramolecular hydrophosphinations of phosphinoalkenes and phosphinoalkynes catalysed by lanthanide complexes give a number of phospholanes and phosphinanes with high yields.^[144] Based

on mechanistic study, the reaction proceeds via P-H oxidative addition followed by a 1,2-insertion and then σ -bond metathesis (Scheme 1.33).

Scheme 1.33 Proposed mechanism for intramolecular hydrophosphinations of phosphinoalkenes and phosphinoalkynes.

Zr-catalysed hydrophosphination of alkenes with primary phosphine was reported recently (Scheme 1.34).^[145] The anti-Markovnikov products (secondary phosphines) are formed with high yields at ambient temperature.

Scheme 1.34 Zr-catalysed hydrophosphination of alkenes.

A new Pd-catalysed hydrophosphonylation of alkenes with dialkyl H-phosphonates was developed recently (Scheme 1.35).^[146] This provides an alternative route to the synthesis of phosphonates from unreactive dialkyl H-phosphonates and alkenes with moderate to good yields.

Scheme 1.35 Pd-catalysed hydrophosphonylation of alkenes with dialkyl H-phosphonates.

A simple hydrophosphinylation of alkenes with hypophosphites catalysed by NiCl_2 at room temperature was investigated (Scheme 1.36).^[147] H-phosphinates are formed with moderate to good isolated yields. This hydrophosphination can be combined with other reactions in a one-pot manner to give other organophosphorus compounds.

Scheme 1.36 NiCl_2 -catalysed hydrophosphinylation of alkenes with hypophosphites

Fe-catalysed hydrophosphinations are a growing area of research due to iron's abundance and as a greener metal. A simple and very low catalytic loading Fe-catalysed hydrophosphination at room temperature was reported (Scheme 1.37).^[148] Tertiary phosphines are formed with moderate to high yields.

Scheme 1.37 Hydrophosphination catalysed by salen-Fe complex.

Apart from the traditional homogeneous metal catalysed hydrophosphinations, solid-supported metal catalyst and micellar catalyst have been developed.^[149-152]

Regioselectivity can generally be achieved by adding catalytic amount of acid (in the case of Ni and Pd catalysis) and by changing the ligands and solvents.^[153-154] Recently, it was found that the oxidation state of metal catalyst can also influence the regioselectivity. FeCl₂ and FeCl₃ give anti-Markovnikov and Markovnikov products respectively (Scheme 1.38).^[155] The main reason for this selection is still unclear but it might be due to the Lewis acidity of the metal centre.

Scheme 1.38 Regioselective hydrophosphination catalysed by FeCl₂ and FeCl₃.

1,4-hydrophosphination of 1,3-dienes by Ti catalyst was also reported (Scheme 1.39).^[156]

Allylic phosphine sulphides were formed with excellent yields.

Scheme 1.39 Ti-catalysed 1,4-hydrophosphination of 1,3-dienes.

1,2-diphosphines and related compounds can be synthesised via double hydrophosphinations (Scheme 1.40).^[157-160] This method is an alternative for forming bidentate PP ligands.

Scheme 1.40 Metal-catalysed double hydrophosphinations.

Chiral phosphines and derivatives can be synthesised via asymmetric hydrophosphinations. Enantiopure P-chiral phosphines are difficult to synthesise via asymmetric hydrophosphinations.^[125] However, this can be achieved by using chiral palladacycle and Pd PCP pincer complex (Scheme 1.41).^[161-162]

Scheme 1.41 Synthesis of P-chiral phosphines and derivatives from asymmetric hydrophosphination.

On the other hand, C-chiral phosphines and derivatives, phosphinanes and diphosphines can easily be synthesised via chiral palladacycles (Scheme 1.42), Pd PCP-pincer complexes (Scheme 1.43) and chiral Zn complexes (Scheme 1.44).^[163-166]

Scheme 1.42 Asymmetric hydrophosphination catalysed by chiral palladacycles.

Scheme 1.43 Asymmetric hydrophosphination catalysed by chiral Pd PCP pincer complex.

Scheme 1.44 Asymmetric hydrophosphination catalysed by chiral Zn complexes.

Metal-catalysed asymmetric Pudovik reactions produce chiral α -hydroxyphosphonates in excellent yields and ee (Scheme 1.45).^[167-168]

Scheme 1.45 Metal-catalysed asymmetric Pudovik reactions.

In short, metal-catalysed hydrophosphinations generally give high to excellent yields of phosphines and derivatives with better control of regio- and stereoselectivity. Chiral phosphines and derivatives can be formed with high yields and ee, particularly via chiral Pd-catalysed reactions. The disadvantages of this method are that only phosphines (and derivatives) and a limited number of phosphinanes and phospholanes can be formed. Also, the metal catalysts are generally not recovered and reused.

1.2.3 Organocatalytic additions of P-H bond onto C-X multiple bonds

Organocatalytic hydrophosphinations is another growing area of research.^[92] Various organocatalysts have been screened for phospho-Michael additions. Proline-derivative catalysed asymmetric hydrophosphination of α,β -unsaturated aldehydes have been reported with high yields and ee (scheme 1.46).^[169]

Scheme 1.46 Asymmetric hydrophosphination of α,β -unsaturated aldehydes catalysed by proline-derivative.

Thiourea- and squaramide-catalysed asymmetric phospho-Michael additions of nitroalkenes and H-phosphonates also give phosphonates in high yields and ee.^[170-171]

Asymmetric organocatalytic phospho-Michael addition of α,β -unsaturated ketones and phospho-Morita–Baylis–Hillman reaction were also investigated.^[172-173] Recently, there is a report on N-heterocyclic carbene (NHC) catalysed hydrophosphination of activated alkenes (Scheme 1.47).^[174]

Scheme 1.47 NHC-catalysed hydrophosphination of activated alkenes.

Asymmetric Pudovik reaction catalysed by squaramide were reported (Scheme 1.48).^[175]

Scheme 1.48 Squaramide-catalysed asymmetric Pudovik reaction.

Asymmetric phospho-Mannich reaction of imines and H-phosphonates catalysed by various organocatalysts were also reported (Scheme 1.49).^[176-179]

Scheme 1.49 A recent example of organocatalysed asymmetric phospho-Mannich reaction.

The advantage of organocatalytic hydrophosphinations is that the reaction is considered to be greener and C-chiral phosphine oxides and phosphonates can be synthesised in high yields and ee. However, large amount of catalysts is usually required and the catalysts are not reused. Also, the carbon substrates are limited to Michael acceptors, aldehydes and imines.

Overall, hydrophosphination is an atom-economy efficient P-C bond synthesis for the syntheses of chiral phosphines and derivatives. However, only a limited variety and number of P-heterocycles, such as phospholanes, phosphinanes and phosphepines, can be synthesised and the catalysts used in these reactions are generally not recycled for use.

1.3 P-C bond formation via metal-catalysed cross-coupling reactions

P-C bond formation via metal-catalysed cross-coupling reactions is a wide area of research.^[35, 121, 180-182] This section is divided into several smaller subsections based on bond types of starting materials and various classes of reactions. The main focus is on special and recent examples.

1.3.1 General metal-catalysed C-X/P-Y cross-couplings

Metal-catalysed cross-couplings C-X (X = halides, O, N, B, CN, CO₂H) bonds with P-Y (Y = H, Si, Cl, P) bonds is the common type of P-C bond synthesis. The general proposed mechanism is very similarly to that of the classic metal-catalysed cross-couplings. There are several reports on metal-catalysed Csp³-X/P-Y cross couplings. C-chiral allylic phosphines and phosphine oxides can be formed via Pd-catalysed enantioselective allylation with high ee (Scheme 1.50).^[183-184]

Scheme 1.50 Pd-catalysed enantioselective allylation of phosphine oxide.

P-chiral phosphines and derivatives can also be synthesised via Csp³-P cross-couplings. Cu-catalysed reaction of ethyl diazoacetate and enantiopure secondary phosphine borane produces enantiopure tertiary phosphine-borane complex in good yields.^[185] P-chiral phosphine and diphosphine species can also be synthesised via Pt- and Ru-catalysed enantioselective coupling of racemic secondary phosphines with alkyl bromides and chlorides respectively (Scheme 1.51 and 1.52).^[186-187]

Scheme 1.51 Pt-catalysed asymmetric alkylation of secondary phosphines.

Scheme 1.52 Ru-catalysed asymmetric coupling of secondary phosphine with alkyl chlorides.

Metal-catalysed $\text{Csp}^2\text{-X/P-Y}$ cross couplings are the most common type of metal-catalysed P-C coupling method. There are many papers on cross-coupling of P-H and $\text{Csp}^2\text{-halide}$ bonds catalysed by Pd, Ni and Cu.^[181, 188-195] Generally, phosphines and its P=O derivatives are formed in high yields. A series of diphosphines have been developed based on this approach (Scheme 1.53).^[196] This method is useful as diphosphine of this type is difficult to synthesise from the dilithiated aryl species since benzophosphole is inevitably formed (ratio of diphosphine to benzophosphole is about 2:1 via organolithium).

Scheme 1.53 Pd-catalysed synthesis of diphosphines.

Several enantioselective Csp²-halide/P-H cross-couplings to form P-chiral phosphines were reported.^[197] Enantioselective syntheses of P-chiral P-heterocycles via Csp²-halide/P-H cross-couplings have also been reported (Scheme 1.54).^[198-199]

Scheme 1.54 Metal-catalysed enantioselective synthesis of P-heterocycles via Csp²-halide/P-H cross-couplings.

Csp²-halide/P-Si cross-couplings also produce phosphines.^[200] Pd-catalysed cross-coupling of silylphosphines and aryl iodides give P-chiral phosphine derivatives with high yields and ee (Scheme 1.55).^[201]

Scheme 1.55 Pd-catalysed enantioselective cross- coupling of silylphosphines and aryl iodides.

Pd-catalysed coupling of Csp^2 -halides and phosphites give arylphosphonates (Scheme 1.56).^[202] This type of P-C bond synthesis is similar to Arbuzov reaction.

Scheme 1.56 Pd-catalysed cross coupling of aryl halides with phosphites.

Metal-catalysed Csp^2 -O/P-H couplings are another common method for making phosphines and derivatives.^[203-205] The advantage of C-O compounds over C-halide compounds in coupling reaction is that these compounds can easily be derived from environment-friendly alcohols. A recent example is the Ni-catalysed C-O/P-H cross-coupling of pivalates and P-H compounds (Scheme 1.58).^[206] This method can produce a variety of both Csp^2 -P and Csp^3 -P phosphines and P=O compounds with yields ranging from 43-98%.

Scheme 1.57 Ni-catalysed Csp^2 -O/P(O)-H cross coupling between pivalates and P(O)-H compounds.

Chiral phosphines and derivatives can also be made via the coupling with chiral $\text{Csp}^2\text{-O}$ compounds with racemic phosphines followed by resolution (Scheme 1.58) and via the direct coupling with chiral P-H species (Scheme 1.59).^[207-209]

Scheme 1.58 Synthesis of chiral phosphine boranes from Ni-catalysed $\text{Csp}^2\text{-O/P-H}$ coupling.

Scheme 1.59 Pd-catalysed $\text{Csp}^2\text{-O/P-H}$ coupling between P-chiral phosphine boranes and enol phosphates.

Metal-catalysed $\text{Csp}^2\text{-B/P-H}$ and $\text{Csp}^2\text{-Bi/P-H}$ cross couplings were reported recently.^[210-213] $\text{Csp}^2\text{-N/P-H}$ cross-coupling of arylhydrazines and arldoazonium salts with H-phosphonates were also published recently.^[214-215] The recent cross-couplings of $\text{Csp}^2\text{-CO}_2\text{H}$ and $\text{Csp}^2\text{-CN}$ with P-H bonds demonstrate that alkenyl carboxylic acids and aryl nitrile can also be used to synthesis $\text{Csp}^2\text{-P}$ bonds (Scheme 1.60).^[216-217]

Scheme 1.60 Metal-catalysed Csp²-C/P-H cross-coupling reactions.

There are a limited number of metal-catalysed Csp-X/P-Y couplings. Synthesis of alkynyl phosphine borane via Cu-catalysed cross coupling of alkynyl bromide with secondary phosphine borane has been recently reported by Gaumont (Scheme 1.61).^[218-219]

Scheme 1.61 Cu-catalysed cross coupling of secondary phosphine boranes with alkynyl bromides.

Cross-couplings of chlorophosphines and related compounds with terminal alkynes catalysed by Cu and Ni have also been studied and used in syntheses of bulky alkynylphosphines and bridging diphosphine ligands (Scheme 1.62).^[220-224]

Scheme 1.62 Cu- and Ni-catalysed cross couplings of chlorophosphines and related compounds with terminal alkynes.

Yang's Cu-catalysed P-C bond synthesis (see similar reaction in Scheme 1.60) also works for alkynyl carboxylic acids.^[216] Rh-catalysed cross coupling of terminal alkynes with tetraphenylbiphosphine was also reported.^[225]

In short, many types of phosphines and derivatives can be synthesised via general metal-catalysed cross-coupling reactions. There is a wide substrate scope and P-chiral compounds can be synthesised from racemic starting material with good to excellent ee. These reactions serve as an alternative method for phosphine syntheses as many of these phosphines can be formed more conveniently via the common nucleophilic method. But, in some cases such as the synthesis of biaryl diphosphine, it is more practical to use general metal-catalysed coupling to substantially drive the reaction in the desired way.

1.3.2 Metal-catalysed cross couplings via P-C cleavage

A ring-opening condensation between highly strained cyclopropane and triarylphosphine catalysed by Ni was reported by Wu (Scheme 1.63).^[226] This reaction gives a unique type of bulky phosphines in high yields.

Scheme 1.63 Ni-catalysed ring-opening condensation of triarylphosphines with cyclopropanes.

In 2013, Tobisu and Chatani reported the synthesis of annulated phosphole derivatives from triarylphosphines via Pd-catalysed intramolecular P-C and C-H cleavage (Scheme

1.64).^[227] The advantages of this method are that asymmetric annulated phospholes can be formed and the starting triarylphosphines are easy to synthesise.

Scheme 1.64 Synthesis of annulated phosphole derivatives via Pd-catalysed intramolecular C-H/C-P coupling.

Recently, the same group reported the syntheses of substituted phenoxaphosphines and phenophosphazine derivatives via intramolecular aryl exchange catalysed by Pd (Scheme 1.65).^[228]

Scheme 1.65 Synthesis of 6-membered benzofused phosphacycles via Pd-catalysed intramolecular aryl exchange.

1.3.3 Metal-catalysed C-H/P-H cross couplings

C-H/P-H cross couplings is the second most atom economy efficient method to form P-C bonds, apart from hydrophosphinations and other addition reactions. This type of

coupling is often referred to as dehydrogenative or oxidative coupling. Synthesis of alkynylphosphonates via Cu-catalysed Csp-H/P-H oxidative coupling of terminal alkynes with H-phosphonates was first reported by Han in 2009 (Scheme 1.66).^[229]

Scheme 1.66 Cu-catalysed oxidative coupling of terminal alkynes with H-phosphonates.

A mechanistic study of this reaction was conducted by Zhao.^[230] It was revealed that dioxygen is activated by the Cu(I) species to form Cu_2O_2 species. Proton transfer from the phosphite to the bridging oxygen atom leads to the formation of a P–C bond. This Cu-catalysed reaction has been applied in syntheses.^[231-232]

Csp²-H/P-H oxidative coupling have been extended to the syntheses of phosphines and related compounds containing aryls and heterocycles. Phosphonates containing electron-withdrawing aryl substituents have been synthesised via Ag-catalysed oxidative coupling (Scheme 1.67).^[233]

Scheme 1.67 Ag-catalysed oxidative coupling of arenes containing electron-withdrawing groups with H-phosphonate.

In 2013, two research groups have reported pyridine-directed Pd-catalysed Csp²-H/P-H couplings of aryls with H-phosphonates and secondary phosphine oxides (Scheme 1.68).^[234-235] The reaction proceeds via oxidative addition of the aryl onto Pd to form a 5-membered palladacycle. These compounds are precursors for potential PN bidentate ligands.

Scheme 1.68 Pyridine-directed Pd-catalysed Csp²-H/P-H cross coupling.

Yu recently reported a similar oxidative coupling of benzamides containing 8-aminoquinoline group with H-phosphonates (Scheme 1.69).^[236] The authors confirmed that the reaction does not proceed via radical pathway and they suspected that a Cu³⁺ intermediate was involved. These compounds could potentially be precursors for PNN chelating ligands.

Scheme 1.69 Cu-catalysed oxidative coupling of benzamides with H-phosphonates.

Various metal-catalysed syntheses of heteroarylphosphines and derivatives via Csp²-H/P-

H oxidative couplings have also been reported (Scheme 1.70).^[237-240]

Scheme 1.70 Metal-catalysed oxidative couplings of heterocycles with H-phosphonates and phosphine oxides.

Annulated phospholes oxides can also be formed via Pd-catalysed Csp²-H/P-H oxidative coupling (Scheme 1.71).^[108, 241]

Scheme 1.71 Synthesis of annulated phosphole oxides from Pd-catalysed intramolecular Csp²-H/P-H coupling.

Csp³-H/P-H oxidative couplings are mainly dominated by CDC. CDC of tetrahydroisoquinoline with H-P(O) compounds catalysed by Cu,^[242] Ru/Ir,^[243] Au,^[151, 244] and ZnO have been reported (Scheme 1.72).^[107]

Scheme 1.72 General representation of metal-catalysed CDC of tetrahydroisoquinoline with H-P(O) compounds.

Cu-catalysed oxidative phosphonation of α-amino ketones was reported by Yang (Scheme 1.73).^[245] Imidoylphosphine oxides are obtained with 20-91% yield.

Scheme 1.73 Cu-catalysed cross coupling of α-amino ketones with diphenylphosphine oxide.

A new Cu-catalysed Csp³-H/P-H oxidative-coupling has been reported by Lei very recently (Scheme 1.74).^[246] The reaction is likely to proceed via radical/radical coupling, and various tertiary β -ketophosphine oxides can be obtained via this method.

Scheme 1.74 Cu-catalysed α -phosphorylation of aryl ketone o-acetyloximes.

Benzophospholane can also be formed via intramolecular Csp³-H/P-H coupling (Scheme 1.75).^[247]

Scheme 1.75 Rh-catalysed intramolecular Csp³-H/P-H coupling.

In short, the advantages of metal-catalysed oxidative couplings are that they are highly atom-economy efficient and the carbon substrates are easily available and more environmental friendly. As this method is still in the early developmental stage, stereoselectivity is generally absent and only a few types of P-heterocycles have been synthesised.

1.3.4 Metal-catalysed oxyphosphorylations, cascade cyclisations and other forms of metal-catalysed P-C syntheses

Oxyphosphorylation is the coupling reaction of C-C multiple bonds with H-P compounds which introduces β -keto group in product molecules. This method was first introduced by Ji in 2011 as an alternative to synthesise β -ketophosphonates from alkenes and H-phosphonates (Scheme 1.76).^[248]

Scheme 1.76 Cu/Fe-catalysed oxyphosphorylation of alkenes with H-phosphonates.

Recently, Zhao modified and expanded this method to alkynes and other H-P(O) compounds (Scheme 1.77).^[249]

Scheme 1.77 Ag/Cu-catalysed oxyphosphorylation of alkynes with H-P(O) compounds.

Metal-catalysed cascade cyclisations are attractive synthetic methods as both the P-C bond and the unique substituent ring system can be formed in a one-pot manner. Several Ag-catalysed cascade cyclisations involving H-P(O) compounds have been reported over the past few years and the general reactions are summarised below (Scheme 1.78).^[250-253]

Scheme 1.78 Ag-catalysed cascade cyclisations.

Cu-, Rh- and Ru-catalysed cascade cyclisation has been reported recently (Scheme 1.79).^[254-256]

R^3, R^4 = alkyl, aryl, alkoxy, aryloxy

Scheme 1.79 Other examples of metal-catalysed cascade cyclisations.

P-heterocycles can also be formed via special types of metal-catalysed reaction. Metal-catalysed intramolecular P-C cyclisation via C-H activation produce phospholane and phosphole (Scheme 1.80).^[257-261]

Scheme 1.80 Metal-catalysed intramolecular cyclisations via C-H activation.

Synthesis of 1,3-oxaphospholes by Rh-catalysed coupling of α -diazo- β -dicarbonyl compounds with *t*-BuCP is shown in Scheme 1.81.^[262]

Scheme 1.81 Rh-catalysed synthesis of 1,3-oxaphospholes.

Synthesis of functionalised benzo[*b*]phosphole derivatives via one-pot multicomponent coupling catalysed by Co/Cu was reported by Yoshikai recently (Scheme 1.82).^[263]

Scheme 1.82 Synthesis of benzo[*b*]phospholes via Co/Cu-catalysed multicomponent coupling.

In 2013, Li reported a mild and catalytic phosphonofluorination of unactivated alkenes with H-phosphonate and Selectfluor by silver nitrate (Scheme 1.83).^[264] The reaction produces β -fluorophosphonates in good to excellent yields.

Scheme 1.83 Ag-catalysed phosphonofluorination.

Ag-catalysed carbonphosphonation of α,α -diaryl allylic alcohols was also reported (Scheme 1.84).^[265] The reaction involves a 1,2-aryl migration and formation of a γ -ketone group.

Scheme 1.84 Ag-catalysed carbonphosphonation.

Cu-catalysed synthesis of α -hydroxyphosphonates via cross coupling of H-phosphonates and primary alcohols was reported by Tang.^[266] The α -hydroxyphosphonates were produced in good yields of 36-87%.

Overall, various types of phosphines and derivatives can be synthesised from a wide range of substrates via metal-catalysed cross-couplings. A variety of phospholes and limited number of phospholanes and phenoxaphosphines can also be synthesised. This method serves as an additional to the nucleophilic method as some compounds, such as biaryl diphosphines and phosphonates with unique substituents, are not convenient to synthesise. Limitations of this method are that stereoselectivity is limited only to certain cross-couplings and the catalysts are not recycled for use.

1.4 P-C bond formation via cycloadditions

Cycloaddition is a powerful tool in obtaining P-heterocycles which would otherwise be difficult to synthesise via traditional methods.^[2, 4, 28, 267-268] In this section, a brief introduction to various types of P-C bond forming cycloadditions will be presented with examples.

1.4.1 McCormack reactions

McCormack reaction was first mentioned in U.S. patents in 1953, and was intensively reviewed by Quin.^[6] McCormack reaction is essentially a [1+4] cycloaddition of halophosphine and diene to give a phospholenium cycloadduct which can be converted into either phospholene oxide or phosphole (Scheme 1.85).

Scheme 1.85 McCormack reaction and usual treatments.

Generally bromophosphines are used as some chlorophosphines gives adducts which undergo double bond migration (Scheme 1.86).

Scheme 1.86 Double bond migration issue in chlorophospholenium adduct.

A wide range of phospholenes can be generated from different variety of dienes and halophosphines (Figure 1.1). This method is used mainly to synthesise phospholenes and limited number of phospholes.

Figure 1.1 Examples of McCormack reaction products.

1.4.2 Cycloadditions involving monovalent phosphorous

Electrophilic terminal phosphinidene complex $[RP \rightarrow M(CO)_5]$ are phosphorus analogue of singlet carbenes and they have been used in various cycloadditions to generate a variety of P-heterocycles.^[269-270] They are commonly formed in-situ from 7-phosphanorbornadiene complexes,^[271-272] phosphirane complexes,^[273-274] azaphosphirene complexes,^[275-276] and benzophosphepine complexes (Scheme 1.87).^[130, 277]

Scheme 1.87 Generation of terminal phosphinidene complexes from various precursors.

The detection of transient phosphinidene complex $[\text{Me}_3\text{N}(\text{C}_6\text{H}_4)\text{P}\rightarrow\text{W}(\text{CO})_5]$ in gas-phase mass spectrometric experiments by the group of Lammertsma provides the evidence of the presence of a 'free' phosphinidene complex.^[278]

The first synthesis of phosphirene complexes was reported by Marinetti in 1982 using this method.^[271] The transient $[\text{RP}\rightarrow\text{ML}_n]$ can be trapped via [1+2] and [1+4] cycloadditions with various trapping reagents to give a wide variety of P-heterocycles (Scheme 1.88).^[279-283] The [1+2] cycloaddition of terminal phosphinidene and alkene proceeds via a concerted mechanism as proved by the retention of stereo-configuration of C_2 unit of phosphirane complex.^[284-285]

Scheme 1.88 Trapping reactions of terminal phosphinidene complexes.

Cycloadditions of terminal phosphinidenes with Fischer carbenes also form phosphalkene and P-heterocycles (Scheme 1.89).^[286-287]

Scheme 1.89 Reactions of terminal phosphinidene complexes with Fischer carbenes.

Cycloadditions of $[RP \rightarrow W(CO)_5]$ with silene,^[288] phosphalkenes,^[289] and phosphalkynes give unusual P-heterocycles (Scheme 1.90).^[290-291]

Scheme 1.90 Cycloadditions of terminal phosphinidene complexes with silene, phosphalkenes and phosphalkynes.

In the absence of a trapping reagent, C=C bond containing terminal phosphinidene complexes undergo self-cycloadditions (Scheme1.91).^[292-293]

Scheme 1.91 Self-cycloadditions of terminal phosphinidene complexes.

Chloro-containing allylic phosphinidene complex can also undergo a 1,5-sigmatropic shift to form 1-chlorophosphirane (Scheme1.92).^[294]

Scheme 1.92 Self-rearrangement of allylic phosphinidene complex.

A stepwise building of polyphosphirene chain can also be achieved via stepwise self-cycloadditions of alkynylphosphinidene (Scheme1.93).^[295]

Scheme 1.93 Stepwise building of polyphosphirene.

In short, this method is a versatile method for syntheses of P-heterocycles, particularly phosphirane and phosphirene complexes. However, P-racemic products are formed and trapping reagents must not contain reactive OH and NH to avoid side reactions.

1.4.3 Cycloadditions involving P=C bonds

Compounds containing P=C bonds, such as phosphalkenes, 2*H*-phospholes and phosphinines, can undergo various cycloadditions to form a wide range of P-heterocycles.^[4, 28] This subsection will focus on the special types of cycloadditions involving P=C bonds.

Phosphetane and phosphete complexes can be synthesised via intermolecular and intramolecular [2+2] cycloadditions of phosphalkenes derived from phosph-Wittig reaction (Scheme 1.94).^[296]

Scheme 1.94 Synthesis of phosphetane and phosphete complexes via phospho-Wittig reaction.

[3+2] cycloadditions of P=C bonds yield interesting P-heterocycles adducts and recent examples are shown in scheme 1.95.^[5, 297-298]

Scheme 1.95 [3+2] Cycloadditions of P=C bonds with 1,3-dipolar.

[4+2] cycloadditions are the most common type of P=C cycloadditions as there are many dienes and alkenes/alkynes available.^[267, 283, 299-301] Recent examples are shown in scheme 1.96.

Scheme 1.96 [4+2] Cycloadditions involving P=C bonds.

In short, a variety of P-heterocycles and bicyclic compounds can be synthesised via P=C cycloadditions in good yields. It is generally atom-economy efficient. However, some of the starting materials are not convenient to synthesise and stereoselectivity is essentially absent.

1.4.4 Cycloadditions involving phosphalkynes

The synthesis of the first stable and isolatable phosphalkyne ($t\text{-Bu-C}\equiv\text{P}$) was reported by Becker and Uhl in 1981.^[302] Since then, a number of phosphalkynes have been synthesised and used as basic building blocks for P-heterocycles syntheses via cycloadditions.^[268, 303]

Phosphalkynes react with CRCl carbene in [1+2] cycloaddition to generate 1-chloro-1-phosphirene via a 1,3-chloride shift (Scheme 1.97).^[304-305] This serves as a route to 1-chlorophosphirenes.

Scheme 1.97 [1+2] Cycloaddition of carbenes and phosphalkynes.

2-Phosphino-2*H*-phosphirene can also be formed via [1+2] cycloaddition of phosphalkyne with phosphinocarbene (Scheme 1.98).^[306-307]

Scheme 1.98 [1+2] Cycloaddition of phosphinocarbene and phosphalkyne.

Phosphalkynes react with phosphalkenes to give 1,2-dihydro-1,3-diphosphetes via [2+2] cycloadditions (Scheme 1.99).^[308-309]

[4+2] cycloadditions of phosphalkynes with various reagents have also been investigated.

The first products are usually unstable and will undergo further reactions (Scheme 1.101).^[314-321]

Scheme 1.101 Various [4+2] cycloadditions of phosphalkynes.

Interesting compounds such as 2-Dewar phosphinines can also be formed via [4+2] cycloaddition of phosphalkynes (Scheme 1.102).^[322-323]

Scheme 1.102 Synthesis of 2-Dewar phosphinines.

Phosphaalkyne also reacts with Fischer carbenes in Dötz reactions to form P-heterocycles (Scheme 1.103).^[324-326]

Scheme 1.103 Dötz reactions of phosphaalkyne.

Trimerisations of phosphaalkynes to 1,3,5-triphosphabenzene have also been reported (Scheme 1.104).^[327] Cyclodimerisations of phosphaalkynes in coordination spheres of metal complexes produce η^4 -1,3-diphosphacyclobutadiene complexes (Scheme 1.105).^[268]

Scheme 1.104 Trimerisations of phosphalkynes.

Scheme 1.105 Cyclodimerisations of phosphalkyne in coordination sphere of metal complexes.

Recently, phosphaehtynolate ($\text{P}\equiv\text{CO}^-$) has been shown to participate in cycloadditions like traditional phosphalkynes to form various P-heterocycles (Scheme 1.106).^[328-329]

Scheme 1.106 Cycloadditions involving phosphoethynolate.

Overall, cycloadditions are useful and powerful method for synthesising a wide range of normal and unique P-heterocycles in moderate to high yields. These reactions are generally high atom-economy efficient. However, P-racemic products (i.e. phospholenes, phospholes, phosphiranes and phosphirenes) are generally obtained and many of the reactions required high temperature (>100°C) to take place.

1.5 P-C bond formation via ionic and radical reactions

1.5.1 P-C bond formation via ionic reactions

P-C bonds are formed in special Friedel–Crafts reaction of aromatic rings with phosphorus trichloride via phosphonium cation intermediate (Scheme 1.107).^[330-332]

Scheme 1.107 P-C bond formation via special Friedel–Crafts reaction.

Electrophilic substitutions involving phosphiranyl and phosphirenyl cations have also been reported recently (Scheme 1.108).^[333-334] Bulky groups such as ferrocene can be introduced onto P atom of the phosphirane and phosphirene. There is a recent report on electrophilic substitution reactions between phosphirenyl triflate and heterocycles.^[335]

Scheme 1.108 Electrophilic substitutions involving chlorophosphirane and chlorophosphirene complexes.

Electrophilic addition reactions are useful alternative routes in forming P-heterocycles. Various ionic adducts of phosphirenes,^[336-337] and phosphetanes,^[62] can be formed via electrophilic addition reactions of chlorophosphines. Further treatments of these compounds give their respective charge-neutral derivatives (Scheme 1.109).

Scheme 1.109 Formation of ionic adducts of P-heterocycles via electrophilic additions and subsequent conversion reactions.

Formation of 3- and 4-membered P-heterocyclic cations can be formed via electrophilic addition of phosphalkenes (Scheme 1.110).^[338]

Scheme 1.110 TfOH-induced electrophilic additions of phosphalkene.

P-C bonds are also formed via ionic C-H insertions. Reactions of stannocene and plumbocene with phosphonium ions give interesting phosphinometallacene cations (Scheme 1.111).^[339]

Scheme 1.111 Insertions of phosphonium ion into C-H bonds of metallocenes.

Various P-C bond formations via C-H insertions facilitated by Lewis acids are shown in Scheme 1.112.^[260, 340-341] Unusual P-heterocyclic salts are formed.

Scheme 1.112 P-C bond formations via C-H insertions facilitated by Lewis acids.

There is a single report on the insertion of phosphonium ions into cyclopropanes to form phosphetane derivatives (Scheme 1.113).^[342]

Scheme 1.113 P-C bond synthesis via insertion of phosphonium ion into C-C bond.

Intramolecular ring expansion can also be induced (Scheme 1.114).^[281]

Scheme 1.114 Ring expansion of phosphirene complex via electrophilic substitution.

Overall, the ionic P-C synthesis is used mainly to synthesise phosphetanes, although unusual organophosphorus salts can also be formed.

1.5.2 P-C bond formation via radical reactions

Several radical P-C bond formations have been mentioned in earlier sections (i.e. hydrophosphinations and metal-catalysed reactions). In this subsection, examples of the remaining useful radical P-C bond formations will be illustrated. AIBN and related compounds have been widely used as radical initiators in P-C bond synthesis.^[343] A one-pot three-component alkylphosphanylation of olefins and hydrophosphonylative cyclisation of dienes initiated by V-40 and AIBN respectively have been reported (Scheme 1.115).^[344-345]

Scheme 1.115 Radical P-C bond syntheses initiated by V-40 and AIBN.

Ag-mediated CDC reactions of secondary phosphine oxides with benzothiazoles and thiazoles,^[346] and of H-phosphonates with indoles have been published.^[347] In 2013, two independent groups reported the synthesis of benzo[*b*]phosphole oxides in moderate to excellent yields via Ag-mediated dehydrogenative annulation of secondary phosphine oxides with disubstituted acetylenes (Scheme 1.116).^[348-349] This method has great

potential for synthesising a wide range of benzo[*b*]phospholes from easily accessible starting materials.

Scheme 1.116 Synthesis of benzo[*b*]phosphole oxides via Ag-mediated dehydrogenative annulations.

Other Ag-mediated radical P-C bond formations are shown in Scheme 1.117.^[350-351] New functional groups are formed together with P-C bond.

Scheme 1.117 Other Ag-mediated radical P-C bond formations.

There are several Mn-mediated radical P-C bond syntheses,^[352] and recent examples are shown in Scheme 1.118.^[353-354] Phosphine oxides and phosphonates are generally formed.

Scheme 1.118 Mn-mediated radical acetoxyposphorylation of styrenes and alkenyl Csp²-P bond formation.

K₂S₂O₈-mediated oxidative arylphosphination of activated N-substituted-N-arylacrylamide derivatives was reported (Scheme 1.119).^[355]

Scheme 1.119 K₂S₂O₈-mediated radical P-C bond formations.

Overall, the general radical reaction is used to form phosphines and derivatives in moderate to high yields. Ring system can be formed together with the P-C bond, and benzophospholes can be synthesised. However, stereoselectivity and variety of P-heterocycle synthesis are limited.

1.6 Other methods of forming P-C bonds

Terminal phosphinidene complexes are able to insert into C-Z bonds (Z = P, N, Ni) to form new P-C bonds.^[281, 356] The most interesting insertion that [RP→W(CO)₅] can undergo is the C-H insertions which form new P-C bonds (Scheme 1.120).^[357]

Scheme 1.120 Intermolecular C-H insertions of terminal phosphinidene complexes.

Mathey recently reported the synthesis of a series of annulated phosphole complexes via intramolecular phosphinidene C-H insertion (Scheme 1.121).^[358] The 1*H*-phosphole complexes are formed in good to high yields and can be further functionalised.

Scheme 1.121 Intramolecular C-H insertions of terminal phosphinidene complexes.

Examples of P-C bond formations via other C-H activations are shown in scheme 1.122.^[359-360]

Scheme 1.122 Other examples of P-C bond syntheses via C-H activations.

CO insertions into phosphirene complexes forms phosphorus analogue of unsaturated β -lactams (Scheme 1.123).^[361-362]

Scheme 1.123 Syntheses of phosphorus analogue of unsaturated β -lactams via CO insertions.

P-C bonds are formed when frustrated Lewis pairs (FLP) react with simple molecules, such as CO_2 and acetylenes, to form FLP adducts.^[363-367] There is a recent paper on a new method of forming P-C bond reported by Doherty and Westcott (Scheme 1.124).^[368]

Scheme 1.124 Phosphinoboration reaction.

This phosphinoboration reaction is a versatile method for synthesising α -boronate phosphines from a wide range of aldehydes, ketones, aldimines, and α,β -unsaturated enones.

1.7 Summary

Due to the importance of organophosphorus compounds in chemistry, various phosphorus-carbon bond syntheses have been developed. The nucleophilic substitution method is a highly versatile and straightforward method which is commonly used to synthesise a wide range of phosphines and P-heterocycles in good to excellent yields. Hydrophosphination is an atom-economy efficient P-C bond synthesis for the syntheses of chiral phosphines and derivatives. Metal-catalysed cross-couplings provide alternative routes to the synthesis of phosphines and common P-heterocycles. Cycloaddition reactions of terminal phosphinidene complexes, P=C and P $\equiv$ C bonds are useful methods for generating a vast variety of P-heterocycles. Other methods such as ionic and radical P-C bond formations and C-H insertions serve as alternative routes to several organophosphorus compounds. Most of these methods utilise the conversion of P(III)/P(V) species to other P(III)/P(V) species. There are limited types of P-C bond syntheses involving a change in the oxidation state of phosphorus, and thus it would be interesting to seek and investigate a new type of P-C bond that has this feature.

1.8 References

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Chapter 2

Using Monovalent Phosphorus Compounds to Form P-C Bonds

2.1 Introduction

Electrophilic terminal phosphinidene complexes $[RP \rightarrow ML_n]$ are phosphorus analogues of singlet carbenes, and they serve as basic building blocks for synthesising a variety of organophosphorus compounds.^[1-2] Evidence of the presence of a 'free' phosphinidene complex generated was obtained via the detection of transient phosphinidene complex $[Me_3N(C_6H_4)P \rightarrow W(CO)_5]$ in gas-phase mass spectrometric experiments.^[3] There are several common ways of generating $[RP \rightarrow W(CO)_5]$.^[4] 7-Phosphanorbornadiene complex **11** is the most common precursor for terminal phosphinidene complexes (Scheme 2.1) due to the ease of functionalising the R group on **11**.^[5-8]

Scheme 2.1 Generation of electrophilic terminal phosphinidene complex from **11**.

P-C bond formations involving $[RP \rightarrow W(CO)_5]$ are limited mostly to cycloadditions, and only a few C-H insertions of phosphinidene complexes are known.^[4] The conversion of P(I) species into P(III) species in these P-C bond syntheses makes them unique synthetic methods as most of the existing methods rely on the conversion of P(III)/P(V) species to another P(III)/P(V) species. Thus it would be interesting to use the reactions of $[RP \rightarrow W(CO)_5]$ and carbon

nucleophiles to create a new type of P-C single bond formation based on P(I) to P(III) conversion.

According to the unpublished results of Marinetti and Mathey, strong nucleophiles such as organolithium and Grignard reagents are incompatible with **11** as they prefer to attack the C=C and C=O bonds of these compounds leading to decompositions (Figure 2.1).

Figure 2.1 Possible sites of nucleophilic attacks on complex **11**.

Hence it is necessary to use softer carbon nucleophiles. Mild nucleophiles such as malonate anions,^[9] and stabilised phosphorus ylides are able to react with **11** to form P-C bonds (Scheme 2.2).^[10-12]

Scheme 2.2 Reaction of **11** with malonate anion and phosphorus ylide.

Although these reactions show that P-C bond can be synthesised via reaction of **11** with mild carbon nucleophiles, their usefulness is limited by the scope of the carbon nucleophiles (in the case of malonate) and the generation of several side products (in the case of phosphorus ylides). Since C-C bond formation is a very vibrant area of research and numerous metal-catalysed C-C bond synthesis methods have been developed,^[13-26] this prompted us to take a closer look at the mild carbon nucleophiles used in these reactions for the possibility of using them to react with $[RP \rightarrow W(CO)_5]$ to form P-C bonds.

2.2 Results and Discussion

We began the investigation by screening the reaction of **11a** with various sources of common soft carbon nucleophiles which are used in C-C bond syntheses. The results are summarised in Table 2.1. All these reactions were run under strictly anhydrous condition as terminal phosphinidene complexes are known to react readily with water.^[7] The product obtained is secondary phosphine complex **13a**. PhZnBr and NaBPh₄ give low yields (entry 3 and 4) due to possible side reactions with the enone functional group in **11a**. The best result is the reaction of **11a** with phenylboronic acid **12a** in the presence of K₃PO₄ that gives **13a** with a good yield of 48% (entry 5). According to ³¹P NMR monitoring of the reaction mixture, this P-C bond forming reaction is extremely clean; only two peaks (corresponding to **11a** and **13a**) are observed during the course of reaction.

	Reagents	Reaction conditions	Yield of 13a (%)
1	PhSnBu ₃ + CsF	THF, 110 °C, 23 h	0
2	PhSnBu ₃	THF, 110 °C, 40 h	0
3	PhZnBr	THF, 50 °C, 1 h	7
4	NaBPh ₄	THF, 110 °C, 30 h	15
5	12a PhB(OH) ₂ + K ₃ PO ₄	Toluene, 110 °C, 17 h	48

Table 2.1 Reactions of **11a** with various sources of soft carbon nucleophiles.

The next step was to optimise this reaction. Bases such as potassium carbonate, potassium *tert*-butoxide and trimethylamine were tested, but they are inefficient and potassium phosphate seems to be the best base for the reaction. Catalysts such as CuCl and [Pd₂(dba)₃] lower the yield and induce the formation of side products. Doubling the amount of boronic acid and base does not increase the yield. This general reaction was then extended to various 7-phosphanorbornadiene complexes **11** and arylboronic acids **12** (Table 2.2). The products are secondary phosphine complexes and the yields are generally around 50%. The structure of **13b** was further confirmed by X-ray crystallography (Figure 2.2).

11 R	12 Ar	Reaction time (h)	13 Yield (%)
11a Ph	12 a Ph	17	13a 48
11a Ph	12 b 2-Th	17	13b 76
11a Ph	12 c 2-Fu	17	13c 46
11a Ph	12 d 4-MeO-C ₆ H ₄	17	13d 52
11b Me	12 a Ph	24	13e 46
11b Me	12 b 2-Th	24	13f 69
11b Me	12 c 2-Fu	17	13g 38
11b Me	12 d 4-MeO-C ₆ H ₄	16	13h 45
11c Bn	12 a Ph	18	13i 52
11c Bn	12 b 2-Th	18	13j 65
11d CH ₂ CH ₂ Cl	12 b 2-Th	24	13k 35
11e OMe	12 a Ph	3	13l 10

Table 2.2 Reaction of 7-phosphanorbornadiene complexes **11** with arylboronic acids **12** in the presence of K_3PO_4 . Th = thienyl, Fu = furyl.

Next we investigated the likelihood of using alkoxy- and aminophosphinidenes in this new P-C bond synthesis. Reaction of methoxyphosphinidene complex, generated from **11e**, with arylboronic acids in presence of potassium phosphate was carried out (Scheme 2.4). The results are less satisfactory than that of aryl- and alkylphosphinidenes. Dithienylphosphine complex **16** is formed when thienylboronic acid was used. The structure of **16** was confirmed by X-ray crystal (Figure 2.3). This could be due to the higher reactivity of thienylboronic acid that lead to the coordination of oxygen atom of the P-OMe bond to the boron reagent which results in the substitution by the thienyl group from another molecule of thienylboronic acid (since three mole equivalent of boronic acid was used).

Scheme 2.4 Reaction of methoxyphosphanorbornadiene complex **11e** with arylboronic acids in the presence of K_3PO_4 .

Figure 2.3 X-ray crystal structure of **16**. Main bond lengths (Å) and angles (deg): P-W 2.4810(7), P-C6 1.808(4), P-C10 1.792(3); C6-P-C10 103.03(15), C6-P-W 116.46(14), C10-P-W 117.78(10).

Similarly, using aminophosphirane **17** as the aminophosphinidene precursor, mixtures of complexes are obtained due to the high reactivity of P-N bond (Scheme 2.5). The yields were determined based on product isolation.

Scheme 2.5 Reaction of aminophosphirane **17** with arylboronic acids in the presence of K_3PO_4 .

Reaction of **17** with sodium tetraphenylborate gives a cleaner reaction (Scheme 2.6).

Scheme 2.6 Reaction of **17** with sodium tetraphenylborate.

Alkylboronic acids were tested for use in this new P-C bond synthesis. Surprisingly, primary phosphine complex **21** is obtained when **11a** is reacted with both methyl- and ethylboronic acids (Scheme 2.7). This indicates that alkyl groups cannot be introduced onto the phosphinidene complex with the use of alkylboronic acids via our P-C bond synthesis.

Scheme 2.7 Reaction of **11a** with alkylboronic acids in the presence of K_3PO_4 .

Next, the effect of aryl substituents on the yields of this new arylation reaction was investigated. The reactions of **11a** and **b** with a range of *ortho*-substituted phenylboronic acids were carried out and the results are summarised in Scheme 2.8.

Scheme 2.8 Effects of *ortho*-substituents on the yields of arylation reaction.

The negative steric effect of *ortho*-substitution is clear. As the size of R' increases from H to Ph, the yields drop drastically from 48% to 0%. The positive electronic effect of 2-ethoxy group is rather clear since it nearly overcomes the negative steric effect. The electronic effect of *para*-substituted phenylboronic acids was also investigated (Scheme 2.9).

Scheme 2.9 Effects of *para*-substituents on the yields of arylation reaction.

The electron-donating *p*-MeO substituent boosts the yield of reaction slightly while electron-withdrawing *p*-CHO, *p*-CN and *p*-B(OH)₂ substituents completely stop the reaction. The

results from these experiments indicate that the arylation reaction is very sensitive to steric hindrance and electronic properties of the substituents on the aryl ring of the boronic acid.

With the basic experimental information about this new P-C synthesis established, we can now discuss the advantage/feature and limitations of this method. The main advantage of our new P-C bond synthesis is its great potential in synthesising a variety of secondary phosphines complexes and simple cyclic ring system such as phosphirane complexes in moderate yields, as it can utilise the wide range of aryl and heteroarylboronic acids developed for Suzuki cross-couplings and the numerous electrophilic phosphinidene complexes developed. This synthesis also involves the rare conversion of P(I) compounds into P(III) compounds. Chirality could also be potentially introduced in the form of R groups on phosphinidene complex or arylboronic acid, and the P-chiral products could then be isolated as diastereomers. However the yields of our method are generally around 50% with practically no enantioselectivity. Also, the reaction works well only with alkyl- and arylphosphinidene complexes and with arylboronic acids which have small and non-electron-withdrawing aryl substituents. These factors make our synthesis less attractive for phosphine syntheses as existing methods such as the usual nucleophilic substitutions, hydrophosphinations and cross-couplings have high yields, wider substrate scopes and, in many cases, high enantioselectivity.^[27-32]

We then began to investigate the mechanism behind this new P-C bond formation by presuming the nucleophile to be the boronate formed from the combination of boronic acid and phosphate. There are two possible mechanistic routes for the formation of **13** from **11**. The first route is a direct nucleophilic attack on the phosphorus centre of **11** and the second

route is the nucleophilic attack on $[RP \rightarrow W(CO)_5]$ generated from **11**. The possibility of the first route was tested. 7-Phosphanorbornene complex **22** was chosen for the test as it is structurally similar to **11a** and it does not generate $[PhP \rightarrow W(CO)_5]$. There is no reaction between **22** with phenylboronic acid in presence of potassium phosphate (Scheme 2.10).

Scheme 2.10 Attempted reaction of **22** with phenylboronic acid in presence of K_3PO_4 .

This indicates that the arylation reaction involving **11** is unlikely to proceed via direct nucleophilic attack of 7-phosphanorbornadiene complex by a boronate.

The second possible mechanistic route was investigated. Firstly, the reactions of **11a** with diphenylacetylene and styrene were carried out in the presence and absence of K_3PO_4 to find out the effect of base on the electrophilicity of terminal phosphinidene complex (Scheme 2.11). ^{31}P NMR indicates that phosphirane and phosphirene complexes are the only phosphorus products observed throughout the reaction.

Scheme 2.11 [2+1] Cycloadditions in the presence and absence of K_3PO_4 .

The results indicate that the phosphate does not eliminate the electrophilicity of $[RP \rightarrow W(CO)_5]$ entirely, and the main reason is because of the limited solubility of the phosphate salt in toluene. Nevertheless, the lowered yields obtained in the presence of phosphate suggest there is some interaction between the phosphate and $[RP \rightarrow W(CO)_5]$.

A key finding was made when **11a** was reacted with phenylboronic acid in the absence of K_3PO_4 (Scheme 2.12). **13a** was formed in a lower yield of 14%.

Scheme 2.12 Reaction of **11a** with phenylboronic acid in the absence of K_3PO_4 .

This experiment indicates that the reaction can proceed simply via the reaction of arylboronic acid and **11** and the presumed boronate (adduct of arylboronic acid and phosphate) might not be the actual nucleophile.

This result allowed us to begin the theoretical study of the mechanism by investigating the reaction of phosphinidene and boronic acid. Although the phosphinidene complexes typically behave as classic electrophiles via the empty p-orbital on phosphorus atom, they can exhibit the rare role as nucleophiles via the lone pair on phosphorus atom.^[33-34] To find out how phosphinidene complex could interact with arylboronic acid, DFT calculations at the rB3LYP/6-31G(d)-lanl2dz(W) and rB3LYP/ 6-31G(d) levels were performed for $[MeP \rightarrow W(CO)_5]$ and $PhB(OH)_2$ respectively.^[35] Comparison of the energy differences in the frontier orbitals of $[MeP \rightarrow W(CO)_5]$ and $PhB(OH)_2$ suggests that the most likely interaction between

[MeP→W(CO)₅] and PhB(OH)₂ is via the interaction of the oxygen's lone pair (HOMO-1) of PhB(OH)₂ with the empty p-orbital (LUMO) of [MeP→W(CO)₅]. This [MeP-W(CO)₅] + PhB(OH)₂ system was chosen and the computations were performed using DFT at the B3LYP or RB3PW91-Lanl2dz (W) levels. The optimisation led to the B-O bond insertion product of phosphinidene **23**. The computed structure of **23** is shown in Figure 2.4. The P-B bond is a typical single bond with a length of 1.954 Å as compared with the P-B bond length of Ph₃P-BH₃ at 1.917 Å.^[36] The sum of angles at boron is 359.9°. This indicates that the boron is planar and has a vacant p-orbital that strongly participates in the LUMO, as shown in Figure 2.5.

Figure 2.4 Computed structure of the phosphinidene insertion product **23**. Main distances (Å) and angles (deg): P16-B32 1.954, P16-W15 2.504, P16-O19 1.668, P16-C11 1.842, B32-O17 1.359, B32-C21 1.557; W15-P16-B32 115.0, W15-P16-O19 110.5, W15-P16-C11 116.8, B32-P16-O19 106.7, P16-B32-O17 111.9, P16-B32-C21 124.9, O17-B32-C21 123.1; O19-P16-B32-C21 20.3.

Figure 2.5 LUMO (Kohn-Sham) of insertion product **23**.

This reaction is quite similar to the classic insertion of phosphinidene into the O-H bond of water.^[7] **11a** was reacted with excess trimethyl borate to check the possibility of this reaction (Scheme 2.13). Formation of **13l** shows that the insertion of phosphinidene into B-O bond does take place.

Scheme 2.13 Reaction of **11a** with excess trimethyl borate.

Computation on the isomer product **24** was also carried out since its hydrolysis could give **13e**. Its geometry is shown in Figure 2.6.

Figure 2.6 Computed structure of the isomerisation product **24**. Main distances (Å) and angles (deg): P16-B32 1.964, P16-W15 2.556, P16-C21 1.844, P16-C11 1.843, B32-O17 1.358, B32-O19 1.358; W15-P16-B32 114.1, W15-P16-C21 117.0, W15-P16-C11 115.0, B32-P16-C21 101.2, P16-B32-O17 123.9, P16-B32-O19 116.4, O17-B32-O19 119.7; C21-P16-B32-O19 103.2.

The relative energies of **23** and **24** calculated at rB3LYP/6-31G(d)-lanl2dz(W) level are shown in Figure 2.7. The main point is that **24** lies 22.9 kcal mol⁻¹ lower in energy than **23**. This suggests the migration of Ph is favoured over the migration of OH.

Figure 2.7 Relative energy level diagram of possible intermediates **23** and **24** (in kcalmol.⁻¹).

Based on the general mechanism of the Suzuki cross-coupling, we considered that the base (phosphate) coordinates to the boron centre of **23** and increases the nucleophilicity of the phenyl group. This facilitates the intramolecular nucleophilic substitution by the phenyl group onto the P-OH bond to give an analogue of **24**. The current proposed mechanism is illustrated in Scheme 2.14.

Scheme 2.14 Proposed mechanism of arylation reaction of phosphinidene.

According to the study of the isomerisation of 1*H*-phospholes into 2*H*-phospholes,^[37] we think that the ipso carbon of the phenyl ring becomes tetracoordinated during this 1,2-migration from B to P atom. For alkyl group the situation will be complete different. A transient pentacoordinated carbon with much higher energy would be formed during this 1,2-shift. This is unfavourable and thus the reaction does not work with alkylboronic acids.

Although no hydrolysis product of **23** was observed experimentally, one could not rule out the possibility of the hydrolysis of **23** instead of the 1,2-aryl migration based on our proposed mechanism. It could only be hypothesised that the 1,2-shift proceeds faster than the hydrolysis. More computations and experiments are required to improve on the tentative proposed mechanism.

Lastly, we tried to understand how **21** was formed. The reaction of **11a** with methylboronic acid in the absence of potassium phosphate gives **25** and **21** in yield of 50% and 2% respectively (Scheme 2.15). Formation of **25** is anticipated as the hydrolysis product of an analogue of **23**.

Scheme 2.15 Reaction of **11a** with methylboronic acid in the absence of K_3PO_4 .

Next we confirmed that there is no reaction between **25** and methylboronic acid in the presence and absence of phosphate. ^{31}P NMR of reaction mixture in the presence of phosphate only indicates a signal at $\delta +58.9$ ($J_{\text{PW}} = 249$ Hz; $J_{\text{PH}} = 324.1$ Hz) which corresponds to the deprotonated **25** as indicated by the deprotonation of **25** by phosphate [^{31}P $\delta_{\text{toluene}} = +59.5$ ($J_{\text{PW}} = 250$ Hz; $J_{\text{PH}} = 324.1$ Hz)) and NaH [^{31}P $\delta_{\text{THF}} = +55.2$ ($J_{\text{PW}} = 245$ Hz; $J_{\text{PH}} = 319.7$ Hz)]. Similar results were obtained when boric acid was used (Scheme 2.16).

Scheme 2.16 Reaction of **11a** with boric acid in presence and absence of K_3PO_4 .

Unfortunately, these preliminary results provide no explanation for this phenomenon at this moment. The reaction could be an alternative synthetic method for forming primary phosphine complexes from phosphinidene complexes.^[38] Computations and further experiments in the future could help shed some light on the formation of the primary phosphine complex.

2.3 Conclusion

A new P-C bond formation method involving the use of 7-phosphanorbornadiene complexes and arylboronic acids was discovered. This new method involves the rare P(I) to P(III) conversion and it has great potential as it can utilise the wide range of aryl and heteroarylboronic acids developed for Suzuki cross-couplings and the numerous electrophilic phosphinidene complexes developed. The final products are secondary phosphine complex whose P-H bond can be further functionalised. This new arylation reaction was discovered to be highly sensitive to steric hinderance and electronic properties of the substituents on the aryl ring of the boronic acid. Based on preliminary experiments and DFT calculations, the

tentative proposed mechanism for this arylation involves a B-O bond insertion by the phosphinidene complex, followed by an intramolecular nucleophilic substitution of the aryl group onto P-OH bond promoted by potassium phosphate. This 1,2-aryl shift from B to P can only work with aryl groups, thus no alkylated product was formed when alkylboronic acids were used. At the moment, there is no explanation for the formation of the primary phosphine complex.

2.4 Experimental

All reactions were performed under nitrogen using solvents dried by standard methods. NMR spectra were obtained using Bruker AV400 spectrometer operating at 400 MHz for ^1H , 100.64 MHz for ^{13}C , 162.02 MHz for ^{31}P . Spectra were recorded at 298 K either in CDCl_3 or CD_2Cl_2 . All coupling constants (J values) are reported in Hertz (Hz). HRMS spectra were obtained on a Water Q-ToF Premier MS. X-ray crystallographic analyses were performed on a Bruker X8 APEX diffractometer. Silica gel (230–400 mesh) was used for the chromatographic separations. 7-Phosphanorbornadiene complexes (**11a**, **b**, **d** and **e**),^[5, 39-40] phosphirane complex **17**,^[41] 7-phosphanorbornadene complex **22**,^[5] and hydroxyphosphine complex **25** were prepared based on literature.^[7] Commercially available aryl and heteroaryl boronic acids were treated with Dean-Stark apparatus prior to use. Methyl and ethylboronic acids were dried via distillation with acetone.^[42]

General procedure A: Toluene (3 mL) was added to a mixture of 7-phosphanorbornadiene complex **11** (0.3 mmol.), boronic acid (0.9 mmol.) and anhydrous K_3PO_4 (1.2 mmol.) in a pressure tube under nitrogen. The tube was sealed and heated at 110 °C for 3-24 h. Solvent

was evaporated and the residue was strained onto silica. Purification was performed via cold column chromatography (0 °C) with 15:1 hexane-dichloromethane.

General procedure B: Toluene (3 mL) was added to a mixture of **17** (0.3 mmol.), arylboronic acids (0.9 mmol.) and anhydrous K₃PO₄ (250 mg, 1.2 mmol.) in a pressure tube under nitrogen. The tube was sealed and heated at 110 °C for 12-25 h. Solvent was evaporated and the residue was strained onto silica. Purification was performed via cold column chromatography (0 °C) with hexane, followed 20:1 hexane-dichloromethane, and lastly 15:1 hexane-dichloromethane.

General procedure C: THF (9 mL) was added to a mixture of **17** (475 mg, 1 mmol.) and sodium tetraphenylborate (342 mg, 1 mmol.) in a pressure tube under nitrogen. The tube was sealed and heated at 100 °C for 9 h. THF was evaporated and the residue was strained onto silica. Purification was performed via cold column chromatography (0 °C) with 20:1 hexane-dichloromethane, followed by 15:1 hexane-dichloromethane.

Reactions involving 22 and formation of 21 and 25. General procedure A with respective boron compounds and with/without potassium phosphate. Yields are given in Scheme 2.16 and 2.17.

Synthesis of 1,2,3-triphenylphosphirene and 2-phenylphosphirane Complexes.^[6, 43] Toluene (3 mL) was added to a mixture of **11a** (200 mg, 0.3 mmol.) and diphenylacetylene (or styrene) (1.2 mmol.) in a pressure tube. The tube was sealed and heated at 110 °C for 21 h. Solvent was evaporated and the residue was strained onto silica. Purification was performed via cold column chromatography (0 °C) with 15:1 hexane-dichloromethane. Reaction was repeated in

the presence of dry potassium phosphate (260 mg, 1.2 mmol.). Yields are given in Scheme 2.11.

*Reaction of **11a** with phenylboronic acid.* Toluene (3 mL) was added to a mixture of **11a** (200 mg, 0.3 mmol.), phenylboronic acid (187 mg, 1.5 mmol.) in a pressure tube under nitrogen. The tube was sealed and heated at 110 °C for 18 h. Solvent was evaporated and the residue was strained onto silica. Purification was performed via cold column chromatography (0 °C) with 15:1 hexane-dichloromethane. White solid (22 mg) was obtained. Yield of **13a** is 14%.

*Reaction of **11a** with trimethyl borate.* Excess B(OMe)₃ (1 mL) was added to a toluene solution (2 mL) of **11a** (200 mg, 0.3 mmol.) in a pressure tube under nitrogen. The mixture was heated with stirring at 110 °C for 20 h. Solvent was evaporated and the residue was strained onto silica. Purification was performed via cold column chromatography (0 °C) with 15:1 hexane-dichloromethane. Yield of **13l** is 16%. Reaction was repeated in the presence of dry potassium phosphate (260 mg, 1.2 mmol.) and the yield of **13l** is 20%.

Synthesis of **11c**: Lithium wires were added to DMPP (3 mL, 15.9 mmol) in THF (40 mL). Mixture was stirred for 5 h (³¹P NMR: +55.3 ppm). *Tert*-butylchloride (1.75 mL, 15.9 mmol) was added and stirred at 60°C for 1h. W(CO)₆ (5.00 g, 14.3 mmol) was added and the mixture was stirred overnight (³¹P NMR: −54.1 ppm). Benzyl bromide (1.7 mL, 14.3 mmol) was added and stirred for 1 h. THF was evaporated and the residue was strained onto silica. Purification was performed via column chromatography with hexane. Yellow solids (3.8 g) were obtained

with a yield of 45%. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ +7.3 ($^1J_{\text{PW}} = 212$ Hz). ^1H NMR (CD_2Cl_2): δ 2.04 (s, 6H, Me), 3.36 (d, $^2J_{\text{PH}} = 7.3$ Hz, 2H, CH_2), 6.35 (d, $^2J_{\text{PH}} = 36.7$ Hz, 2H, $\text{PCH}=\text{C}$), 7.11-7.28 (m, 5H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 17.28 (d, $^3J_{\text{CP}} = 11.0$ Hz, Me), 38.39 (d, $^1J_{\text{CP}} = 19.8$ Hz, CH_2), 127.16 (d, $J_{\text{CP}} = 3.1$ Hz, Ph), 128.39 (d, $J_{\text{CP}} = 2.6$ Hz, Ph), 129.10 (d, $^1J_{\text{CP}} = 41.4$ Hz, $\text{PC}=\text{C}$), 129.88 (d, $J_{\text{CP}} = 4.7$ Hz, Ph), 135.06 (d, $^2J_{\text{CP}} = 7.3$ Hz, Ph ipso), 152.07 (d, $^2J_{\text{CP}} = 3.1$ Hz, $\text{PC}=\text{C}$), 196.68 (d, $^2J_{\text{CP}} = 6.7$ Hz, cis CO), 199.84 (d, $^2J_{\text{CP}} = 18.6$ Hz, trans CO). HRMS: m/z 526.0172 (calcd for $\text{C}_{18}\text{H}_{15}\text{O}_5\text{PW}$ 526.0167). Benzylphosphole-tungsten complex (3.8 g, 7.22 mmol) and DMAD (8 mL, 65.1 mmol) were dissolved in toluene (30 mL) and stirred at 87°C for 24h. Toluene was evaporated and the residue was strained onto silica. Purification was performed via column chromatography with 5:1 hexane-ethyl acetate. Bright yellow solids (2.1 g) were obtained with a yield of 44%. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ +210.8 ($^1J_{\text{PW}} = 241$ Hz). ^1H NMR (CD_2Cl_2): δ 1.99 (d, $^4J_{\text{PH}} = 1.4$ Hz, 6H, Me), 3.71 (d, $^2J_{\text{PH}} = 4.4$ Hz, 2H, CH_2), 3.74 (d, $^2J_{\text{PH}} = 2.5$ Hz, 2H, CH), 3.82 (s, 6H, OMe), 7.22-7.34 (m, 5H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 16.10 (d, $^3J_{\text{CP}} = 2.1$ Hz, Me), 42.54 (d, $^1J_{\text{CP}} = 2.1$ Hz, CH_2), 52.82 (s, OMe), 60.48 (d, $^1J_{\text{CP}} = 18.3$ Hz, PCH), 127.45 (d, $J_{\text{CP}} = 2.1$ Hz, Ph), 129.39 (s, Ph para), 130.18 (d, $J_{\text{CP}} = 4.9$ Hz, Ph), 134.77 (d, $^2J_{\text{CP}} = 1.6$ Hz, Ph ipso), 139.61 (d, $^2J_{\text{CP}} = 16.3$ Hz, $\text{C}-\text{Me}$), 146.03 (d, $^2J_{\text{CP}} = 4.6$ Hz, $\text{C}-\text{CO}_2$), 165.56 (d, $^3J_{\text{CP}} = 2.9$ Hz, CO_2), 196.40 (d, $^2J_{\text{CP}} = 6.5$ Hz, cis CO), 198.17 (d, $^2J_{\text{CP}} = 26.8$ Hz, trans CO). HRMS: m/z 668.0325 (calcd for $\text{C}_{24}\text{H}_{21}\text{O}_9\text{PW}$ 668.0433).

Synthesis of **13a**: General Procedure A (17 h). White solids obtained with a yield of 48 %. ^{31}P NMR (CDCl_3): δ -13.6 ($^1J_{\text{PW}} = 231$ Hz, $^1J_{\text{PH}} = 345$ Hz). ^1H NMR (CDCl_3): δ 6.83 (d, $^1J_{\text{PH}} = 345$ Hz,

1H, PH), 7.42-7.56 (m, 10H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 129.25 (d, $^3J_{\text{CP}} = 10.0$ Hz, Ph, CH), 130.73 (d, $^4J_{\text{CP}} = 2.1$ Hz, Ph, para), 132.48 (d, $^1J_{\text{CP}} = 43.8$ Hz, Ph, ipso), 132.47 (d, $^2J_{\text{CP}} = 11.6$ Hz, Ph, CH), 196.32 (d, $^2J_{\text{CP}} = 6.9$ Hz, cis CO), 199.13 (d, $^2J_{\text{CP}} = 21.2$ Hz, trans CO). HRMS: m/z 509.9857 (calcd for $\text{C}_{17}\text{H}_{11}\text{O}_5\text{PW}$ 509.9854).

Synthesis of **13b**: General Procedure A (17 h). White solids obtained with a yield of 76 %. ^{31}P NMR (CD_2Cl_2): δ -35.8 ($^1J_{\text{PW}} = 234$ Hz, $^1J_{\text{PH}} = 355.2$ Hz). ^1H NMR (CD_2Cl_2): δ 7.11 (d, $^1J_{\text{PH}} = 355.2$ Hz, 1H, PH), 7.22 (ddd, $J = 4.8, 3.8, 1.0$ Hz, 1H, Th), 7.42-7.59 (m, 6H, Ar), 7.72 (ddd, $J = 4.9, 2.4, 1.1$ Hz, 1H, Th). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 129.12 (d, $^3J_{\text{CP}} = 11.1$ Hz, Th, CH), 129.54 (d, $^3J_{\text{CP}} = 10.2$ Hz, Ph, CH), 131.05 (d, $^4J_{\text{CP}} = 2.0$ Hz, Ph, para), 131.67 (d, $^2J_{\text{CP}} = 11.9$ Hz, Ph, CH), 131.23 (d, $^1J_{\text{CP}} = 40.8$ Hz, Ph, ipso), 133.92 (d, $^4J_{\text{CP}} = 2.4$ Hz, Th, CH), 134.37 (d, $^1J_{\text{CP}} = 47.7$ Hz, Th, ipso), 137.52 (d, $^2J_{\text{CP}} = 12.3$ Hz, Th, CH), 196.57 (d, $^2J_{\text{CP}} = 6.9$ Hz, cis CO), 199.33 (d, $^2J_{\text{CP}} = 22.3$ Hz, trans CO). HRMS: m/z 515.9418 (calcd for $\text{C}_{15}\text{H}_9\text{O}_5\text{PSW}$ 515.9418).

Synthesis of **13c**: General Procedure A (17 h). White solids obtained with a yield of 46 %. ^{31}P NMR (CD_2Cl_2): δ -43.1 ($^1J_{\text{PW}} = 234$ Hz, $^1J_{\text{PH}} = 359.0$ Hz). ^1H NMR (CD_2Cl_2): δ 6.54 (m, 1H, Fu, CH), 6.94 (d, $^1J_{\text{PH}} = 359.0$ Hz, 1H, PH), 7.02 (s, 1H, Fu, CH), 7.45-7.56 (m, 5H, Ph), 7.73 (s, 1H, Fu, CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 111.88 (d, $^3J_{\text{CP}} = 7.1$ Hz, Fu, CH), 122.93 (d, $^2J_{\text{CP}} = 19.0$ Hz, Fu, CH), 129.53 (d, $^3J_{\text{CP}} = 10.5$ Hz, Ph, CH), 131.09 (d, $^4J_{\text{CP}} = 2.0$ Hz, Ph, para), 131.75 (d, $^1J_{\text{CP}} = 49.1$

Hz, Ph, ipso), 131.90 (d, $^2J_{CP} = 12.2$ Hz, Ph, CH), 146.89 (d, $^1J_{CP} = 56.1$ Hz, Fu, ipso), 149.04 (d, $^4J_{CP} = 4.3$ Hz, Fu, CH), 196.31 (d, $^2J_{CP} = 6.9$ Hz, cis CO), 199.22 (d, $^2J_{CP} = 22.4$ Hz, trans CO). HRMS: m/z 499.9615 (calcd for C₁₅H₉O₆PW 499.9646).

Synthesis of **13d**: General Procedure A (17 h). White solids obtained with a yield of 52 %. ^{31}P NMR (CD₂Cl₂): δ -16.3 ($^1J_{PW} = 229\text{Hz}$, $^1J_{PH} = 347.8$ Hz). ^1H NMR (CD₂Cl₂): δ 3.83 (s, 3H, OMe), 6.86 (d, $^1J_{PH} = 347.8$ Hz, 1H, PH), 6.99-7.60 (m, 9H, Ar). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD₂Cl₂): δ 55.82 (s, OMe), 115.10 (d, $^3J_{CP} = 11.3$ Hz, Ar, CH), 122.94 (d, $^1J_{CP} = 47.7$ Hz, Ar, ipso), 129.45 (d, $^3J_{CP} = 10.0$ Hz, Ph, CH), 130.74 (d, $^4J_{CP} = 1.9$ Hz, Ph, para), 132.21 (d, $^2J_{CP} = 11.5$ Hz, Ph, CH), 134.17 (d, $^1J_{CP} = 44.0$ Hz, Ph, ipso), 134.96 (d, $^2J_{CP} = 13.2$ Hz, Ar, CH), 162.20 (d, $^4J_{CP} = 1.6$ Hz, Ar, COMe), 196.90 (d, $^2J_{CP} = 6.9$ Hz, cis CO), 199.82 (d, $^2J_{CP} = 21.1$ Hz, trans CO). HRMS: m/z 539.9960 (calcd for C₁₈H₁₃O₆PW 539.9959).

Synthesis of **13e**: General Procedure A (24 h). White solids obtained with a yield of 46 %. ^{31}P NMR (CDCl₃): δ -43.6 ($^1J_{PW} = 227\text{Hz}$, $^1J_{PH} = 340.2$ Hz). ^1H NMR (CDCl₃): δ 1.98 (dd, $^2J_{PH} = 8.2$ Hz, $^3J_{HH} = 6.6$ Hz, 3H, Me), 5.93 (dq, $^1J_{PH} = 340.2$ Hz, $^3J_{HH} = 6.6$ Hz, 1H, PH), 7.43-7.56 (m, 5H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃): δ 14.77 (d, $^1J_{CP} = 28.9$ Hz, Me), 129.26 (d, $^3J_{CP} = 10.0$ Hz, Ph, CH), 130.56 (d, $^4J_{CP} = 2.1$ Hz, Ph, para), 130.99 (d, $^2J_{CP} = 11.0$ Hz, Ph, CH), 133.36 (d, $^1J_{CP} = 45.0$ Hz, Ph,

ipso), 196.39 (d, $^2J_{CP} = 7.0$ Hz, cis CO), 199.38 (d, $^2J_{CP} = 20.8$ Hz, trans CO). HRMS: m/z 447.9699 (calcd for C₁₂H₉O₅PW 447.9697).

Synthesis of **13f**: General Procedure A (24 h). White solids obtained with a yield of 69 %. ^{31}P NMR (CD₂Cl₂): δ -63.8 ($^1J_{PW} = 234$ Hz, $^1J_{PH} = 348.4$ Hz). ^1H NMR (CD₂Cl₂): δ 2.05 (dd, $^2J_{PH} = 8.0$ Hz, $^3J_{HH} = 6.6$ Hz, 3H, Me), 6.25 (dq, $^1J_{PH} = 348.4$ Hz, $^3J_{HH} = 6.5$ Hz, 1H, PH), 7.22 (ddd, $J = 4.8$, 3.7, 1.0 Hz, 1H, Th), 7.48 (dd, $J = 7.5$, 3.5 Hz, 1 H, Th), 7.70 (ddd, $J = 4.9$, 2.5, 1.1 Hz, 1 H, Th). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD₂Cl₂): δ 16.99 (d, $^1J_{CP} = 31.4$ Hz, Me), 128.98 (d, $^3J_{CP} = 10.8$ Hz, Th, CH), 132.63 (d, $^4J_{CP} = 2.5$ Hz, Th, CH), 132.86 (d, $^1J_{CP} = 43.9$ Hz, Th, ipso), 135.82 (d, $^2J_{CP} = 11.4$ Hz, Th, CH), 196.61 (d, $^2J_{CP} = 7.0$ Hz, cis CO), 199.45 (d, $^2J_{CP} = 21.9$ Hz, trans CO). HRMS: m/z 453.9261 (calcd for C₁₀H₇O₅PSW 453.9261).

Synthesis of **13g**: General Procedure A (17 h). Pale yellow oil obtained with a yield of 38 %. ^{31}P NMR (CD₂Cl₂): δ -71.6 ($^1J_{PW} = 231\text{Hz}$, $^1J_{PH} = 351.2$ Hz). ^1H NMR (CD₂Cl₂): δ 1.98 (dd, $^2J_{PH} = 8.2$ Hz, $^3J_{HH} = 6.6$ Hz, 3H, Me), 6.06 (dq, $^1J_{PH} = 351.2$ Hz, $^3J_{HH} = 6.5$ Hz, 1H, PH), 6.53 (m, 1H, Fu, CH), 6.96 (m, 1H, Fu, CH), 7.75 (s, 1H, Fu CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD₂Cl₂): δ 13.09 (d, $^1J_{CP} = 33.0$ Hz, Me), 111.69 (d, $^3J_{CP} = 7.0$ Hz, Fu, CH), 121.20 (d, $^2J_{CP} = 18.8$ Hz, Fu, CH), , 147.47 (d, $^1J_{CP} = 56.8$ Hz, Fu, ipso), 148.48 (d, $^4J_{CP} = 4.3$ Hz, Fu, CH), 196.37 (d, $^2J_{CP} = 7.1$ Hz, cis CO), 199.31 (d, $^2J_{CP} = 21.7$ Hz, trans CO). HRMS: m/z 437.9487 (calcd for C₁₀H₇O₆PW 437.9490).

Synthesis of **13h**: General Procedure A (16 h). Pale yellow solids obtained with a yield of 45 %.

^{31}P NMR (CD_2Cl_2): δ -46.0 ($^1J_{\text{PW}} = 226$ Hz, $^1J_{\text{PH}} = 342.1$ Hz). ^1H NMR (CD_2Cl_2): δ 1.94 (pseudo t, $J = 7.4$ Hz, 3H, Me), 3.84 (s, 3H, OMe), 5.94 (dq, $^1J_{\text{PH}} = 342.1$ Hz, $^3J_{\text{HH}} = 6.6$ Hz, 1H, PH), 7.00 (d, $J = 8.0$ Hz, 2H, CH), 7.51 (dd, $J = 11.2, 8.6$ Hz, 2H, CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 15.48 (d, $^1J_{\text{CP}} = 29.2$ Hz, Me), 55.78 (s, OMe), 115.01 (d, $^3J_{\text{CP}} = 10.9$ Hz, Ar, CH), 124.13 (d, $^1J_{\text{CP}} = 48.8$ Hz, Ar, ipso), 133.27 (d, $^2J_{\text{CP}} = 12.7$ Hz, Ar, CH), 161.87 (d, $^4J_{\text{CP}} = 1.3$ Hz, Ar, $\underline{\text{C}}\text{OMe}$), 196.98 (d, $^2J_{\text{CP}} = 7.2$ Hz, cis CO), 200.11 (d, $^2J_{\text{CP}} = 20.8$ Hz, trans CO). HRMS: m/z 477.9780 (calcd for $\text{C}_{13}\text{H}_{11}\text{O}_6\text{PW}$ 477.9803).

Synthesis of **13i**: General Procedure A (18 h). White solids obtained with a yield of 52 %. ^{31}P NMR (CD_2Cl_2): δ -12.4 ($^1J_{\text{PW}} = 227$ Hz, $^1J_{\text{PH}} = 342.6$ Hz). ^1H NMR (CD_2Cl_2): δ 3.42-3.56 (m, 2H, CH_2), 5.91 (ddd, $^1J_{\text{PH}} = 342.6$ Hz, $^3J_{\text{HH}} = 8.2, 5.1$ Hz, 1H, PH), 6.95-7.44 (m, 10H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 38.24 (d, $^1J_{\text{CP}} = 21.6$ Hz, CH_2), 127.38 (d, $J_{\text{CP}} = 3.0$ Hz, Ph), 129.07 (d, $J_{\text{CP}} = 2.4$ Hz, Ph), 129.26 (d, $J_{\text{CP}} = 9.7$ Hz, Ph), 129.35 (d, $J_{\text{CP}} = 4.7$ Hz, Ph), 130.97 (d, $J_{\text{CP}} = 1.9$ Hz, Ph), 131.85 (d, $^1J_{\text{CP}} = 43.0$ Hz, Ph ipso), 132.62 (d, $J_{\text{CP}} = 10.4$ Hz, Ph), 136.46 (d, $^2J_{\text{CP}} = 8.0$ Hz, Ph ipso), 196.64 (d, $^2J_{\text{CP}} = 6.9$ Hz, cis CO), 199.66 (d, $^2J_{\text{CP}} = 22.1$ Hz, trans CO). HRMS: m/z 524.0006 (calcd for $\text{C}_{18}\text{H}_{13}\text{O}_5\text{PW}$ 524.0010).

Synthesis of **13j**: General Procedure A (18 h). White solids obtained with a yield of 65 %. ^{31}P NMR (CD_2Cl_2): δ -35.6 ($^1J_{\text{PW}} = 234$ Hz, $^1J_{\text{PH}} = 347.9$ Hz). ^1H NMR (CD_2Cl_2): δ 3.50 (m, 2H, CH_2), 6.20 (ddd, $^1J_{\text{PH}} = 347.9$ Hz, $^3J_{\text{HH}} = 8.0, 4.4$ Hz, 1H, PH), 6.97-7.65 (m, 8H, Ar). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 40.19 (d, $^1J_{\text{CP}} = 23.1$ Hz, CH_2), 127.57 (d, $J_{\text{CP}} = 3.1$ Hz, Ar), 128.88 (d, $J_{\text{CP}} = 10.3$ Hz, Ar), 129.14 (d, $J_{\text{CP}} = 2.7$ Hz, Ar), 129.45 (d, $J_{\text{CP}} = 4.9$ Hz, Ar), 130.57 (d, $^1J_{\text{CP}} = 40.6$ Hz, Th ipso), 132.94 (d, $J_{\text{CP}} = 2.2$ Hz, Ar), 136.14 (d, $^2J_{\text{CP}} = 8.0$ Hz, Ph ipso), 136.85 (d, $J_{\text{CP}} = 9.7$ Hz, Ar), 196.47 (d, $^2J_{\text{CP}} = 6.9$ Hz, cis CO), 199.07 (d, $^2J_{\text{CP}} = 23.0$ Hz, trans CO). HRMS: m/z 529.9578 (calcd for $\text{C}_{16}\text{H}_{11}\text{O}_5\text{PSW}$ 529.9574).

Synthesis of **13k**: General Procedure A (24 h). White solids obtained with a yield of 35 %. ^{31}P NMR (CD_2Cl_2): δ -56.1 ($^1J_{\text{PW}} = 234$ Hz, $^1J_{\text{PH}} = 352.3$ Hz). ^1H NMR (CD_2Cl_2): δ 2.62 (m, 2H, PCH_2), 3.60 (m, 2H, CH_2Cl), 6.35 (dt, $^1J_{\text{PH}} = 352.3$ Hz, $^3J_{\text{HH}} = 6.2$ Hz, 1H, PH), 7.25 (ddd, $J = 4.7, 3.7, 0.8$ Hz, 1H, Th), 7.50 (dd, $J = 6.8, 3.4$ Hz, 1H, Th), 7.73 (ddd, $J = 4.8, 2.8, 0.8$ Hz, 1H, Th). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 35.96 (d, $^1J_{\text{CP}} = 24.1$ Hz, PCH_2), 41.68 (d, $^2J_{\text{CP}} = 4.2$ Hz, CH_2Cl), 129.31 (d, $^3J_{\text{CP}} = 10.5$ Hz, Th, CH), 129.33 (d, $^1J_{\text{CP}} = 42.5$ Hz, Th, ipso), 133.25 (d, $^4J_{\text{CP}} = 2.8$ Hz, Th, CH), 136.74 (d, $^2J_{\text{CP}} = 9.3$ Hz, Th, CH), 196.23 (d, $^2J_{\text{CP}} = 6.9$ Hz, cis CO), 198.81 (d, $^2J_{\text{CP}} = 22.7$ Hz, trans CO). HRMS: m/z 501.9016 (calcd for $\text{C}_{11}\text{H}_8\text{O}_5\text{PSCIW}$ 501.9028).

Synthesis of **13l**: General Procedure A (3 h). White solids obtained with a yield of 10 %. ^{31}P NMR (CD_2Cl_2): δ -107.1 ($^1J_{\text{PW}} = 279$ Hz, $^1J_{\text{PH}} = 346.6$ Hz). ^1H NMR (CD_2Cl_2): δ 3.50 (d, $^3J_{\text{PH}} = 12.5$ Hz, 3H, MeO), 7.52-7.65 (m, 5H, Ph), 7.87 (d, $^1J_{\text{PH}} = 346.6$ Hz, 1H, PH). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 60.31 (d, $^2J_{\text{CP}} = 14.6$ Hz, MeO), 129.46 (d, $^3J_{\text{CP}} = 9.2$ Hz, Ph CH), 130.86 (d, $^2J_{\text{CP}} = 11.9$ Hz, Ph CH), 131.98 (d, $^4J_{\text{CP}} = 1.3$ Hz, Ph, para), 135.19 (d, $^1J_{\text{CP}} = 41.2$ Hz, Ph, ipso), 196.13 (d, $^2J_{\text{CP}} = 7.9$ Hz, cis CO), 200.04 (d, $^2J_{\text{CP}} = 25.5$ Hz, trans CO). HRMS: m/z 463.9648 (calcd for $\text{C}_{12}\text{H}_9\text{O}_6\text{PW}$ 463.9646).

Synthesis of **13m**: General Procedure A (17 h). White solid (14 mg, 9% yield) was obtained. ^{31}P NMR (CD_2Cl_2): δ -27.4 ($^1J_{\text{PW}} = 228$ Hz, $^1J_{\text{PH}} = 348.1$ Hz). ^1H NMR (CD_2Cl_2): δ 2.37 (s, 3H, Me), 7.03 (d, $^1J_{\text{PH}} = 348.1$ Hz, 1H, PH), 7.25-7.62 (m, 9H, Ar). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 21.55 (d, $^3J_{\text{CP}} = 6.5$ Hz, CH_3), 126.95 (d, $J_{\text{CP}} = 11.5$ Hz, CH), 129.47 (d, $J_{\text{CP}} = 10.2$ Hz, CH), 131.06 (d, $J_{\text{CP}} = 2.1$ Hz, CH), 131.27 (d, $J_{\text{CP}} = 1.9$ Hz, CH), 131.29 (d, $^1J_{\text{CP}} = 43.6$ Hz, CP), 131.65 (d, $J_{\text{CP}} = 6.8$ Hz, CH), 131.76 (d, $^1J_{\text{CP}} = 42.9$ Hz, CP), 133.51 (d, $J_{\text{CP}} = 12.0$ Hz, CH), 133.89 (d, $J_{\text{CP}} = 16.7$ Hz, CH), 140.11 (d, $^2J_{\text{CP}} = 5.7$ Hz, C-Me), 196.81 (d, $^2J_{\text{CP}} = 6.9$ Hz, cis CO), 199.65 (d, $^2J_{\text{CP}} = 21.5$ Hz, trans CO). HRMS: m/z 524.0015 (calcd for $\text{C}_{18}\text{H}_{13}\text{O}_5\text{PW}$ 524.0010).

Synthesis of **13n**: General Procedure A (17 h). White solid (13 mg, 8% yield) was obtained. ^{31}P NMR (CD_2Cl_2): δ -60.1 ($^1J_{\text{PW}} = 222$ Hz, $^1J_{\text{PH}} = 345.5$ Hz). ^1H NMR (CD_2Cl_2): δ 2.01 (dd, $^2J_{\text{PH}} = 8.0$ Hz, $^3J_{\text{HH}} = 6.6$ Hz, 3H, CH_3), 2.49 (s, 3H, CH_3), 6.03 (dq, $^1J_{\text{PH}} = 345.5$ Hz, $^3J_{\text{HH}} = 6.6$ Hz, 1H, PH), 7.26-7.45 (m, 4H, Ar). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 13.43 (d, $^1J_{\text{CP}} = 29.9$ Hz, P-Me), 21.03 (d, $^3J_{\text{CP}} = 7.2$ Hz, Me), 126.97 (d, $J_{\text{CP}} = 10.2$ Hz, CH), 130.56 (d, $J_{\text{CP}} = 2.0$ Hz, CH), 130.58 (d, $J_{\text{CP}} = 29.5$ Hz, CH), 131.30 (d, $J_{\text{CP}} = 6.9$ Hz, CH), 132.87 (d, $^1J_{\text{CP}} = 43.3$ Hz, CP), 139.15 (d, $^2J_{\text{CP}} = 6.8$ Hz, C-Me), 196.90 (d, $^2J_{\text{CP}} = 7.0$ Hz, cis CO), 200.01 (d, $^2J_{\text{CP}} = 20.3$ Hz, trans CO). HRMS: m/z 461.9877 (calcd for $\text{C}_{13}\text{H}_{11}\text{O}_5\text{PW}$ 461.9854).

Synthesis of **13p**: General Procedure A (17 h). White solid (46 mg, 27% yield) was obtained. ^{31}P NMR (CD_2Cl_2): δ -30.6 ($^1J_{\text{PW}} = 228$ Hz, $^1J_{\text{PH}} = 356.7$ Hz). ^1H NMR (CD_2Cl_2): δ 1.36 (pseudo-td, $^3J_{\text{HH}} = 6.8$ Hz, $J_{\text{HH}} = 2.0$ Hz, 3H, $\text{CH}_3\text{CH}_2\text{O}$), 4.07 (m, 2H, $\text{CH}_3\text{CH}_2\text{O}$), 6.94 (pseudo-dd, $^1J_{\text{PH}} = 356.7$ Hz, $J_{\text{HH}} = 2.5$ Hz, 1H, PH), 6.92-7.71 (m, 9H, Ar). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 14.62 (s, $\text{CH}_3\text{CH}_2\text{O}$), 64.49 (s, $\text{CH}_3\text{CH}_2\text{O}$), 111.76 (d, $J_{\text{CP}} = 4.0$ Hz, CH), 120.91 (d, $^1J_{\text{CP}} = 44.5$ Hz, CP), 121.22 (d, $J_{\text{CP}} = 9.6$ Hz, CH), 129.14 (d, $J_{\text{CP}} = 10.2$ Hz, CH), 130.92 (d, $J_{\text{CP}} = 1.6$ Hz, CH), 131.25 (d, $^1J_{\text{CP}} = 44.4$ Hz, CP), 132.77 (s, CH), 133.19 (d, $J_{\text{CP}} = 8.8$ Hz, CH), 133.98 (d, $J_{\text{CP}} = 11.9$ Hz, CH), 159.09 (d, $^2J_{\text{CP}} = 3.2$ Hz, COCH_2), 197.10 (d, $^2J_{\text{CP}} = 7.0$ Hz, cis CO), 200.17 (d, $^2J_{\text{CP}} = 21.4$ Hz, trans CO). HRMS: m/z 554.0119 (calcd for $\text{C}_{19}\text{H}_{15}\text{O}_6\text{PW}$ 554.0116).

Synthesis of **13q**: General Procedure A (17 h). White solid (80 mg, 40% yield) was obtained.

^{31}P NMR (CD_2Cl_2): δ -57.3 ($^1J_{\text{PW}} = 224\text{ Hz}$, $^1J_{\text{PH}} = 350.2\text{ Hz}$). ^1H NMR (CD_2Cl_2): δ 1.50 (t, $^3J_{\text{HH}} = 6.9\text{ Hz}$, 3H, $\text{CH}_3\text{CH}_2\text{O}$), 2.00 (pseudo t, $^2J_{\text{PH}} = 6.9\text{ Hz}$, 3H, CH_3), 4.14 (m, 2H, $\text{CH}_3\text{CH}_2\text{O}$), 5.95 (dq, $^1J_{\text{PH}} = 350.2\text{ Hz}$, $^3J_{\text{HH}} = 6.5\text{ Hz}$, 1H, PH), 6.93-7.43 (m, 4H, Ar). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 12.41 (d, $^1J_{\text{CP}} = 29.9\text{ Hz}$, P-Me), 14.78 (s, $\text{CH}_3\text{CH}_2\text{O}$), 64.41 (s, $\text{CH}_3\text{CH}_2\text{O}$), 111.54 (d, $J_{\text{CP}} = 4.4\text{ Hz}$, CH), 121.02 (d, $^1J_{\text{CP}} = 45.7\text{ Hz}$, Ar CP), 121.15 (d, $J_{\text{CP}} = 9.1\text{ Hz}$, CH), 131.48 (d, $J_{\text{CP}} = 6.6\text{ Hz}$, CH), 132.44 (d, $J_{\text{CP}} = 1.1\text{ Hz}$, CH), 159.48 (d, $^2J_{\text{CP}} = 4.0\text{ Hz}$, COCH_2), 197.22 (d, $^2J_{\text{CP}} = 7.2\text{ Hz}$, cis CO), 200.17 (d, $^2J_{\text{CP}} = 20.3\text{ Hz}$, trans CO). HRMS: m/z 491.9948 (calcd for $\text{C}_{14}\text{H}_{13}\text{O}_6\text{PW}$ 491.9959).

Synthesis of **14**: General Procedure A (24 h). White solids obtained with a yield of 30 %.

$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ -187.4 ($^1J_{\text{PW}} = 259\text{ Hz}$). ^1H NMR (CDCl_3): δ 1.43 (m, 2H, CH_2), 1.74 (m, 2H, CH_2), 7.39-7.51 (m, 5H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 11.17 (d, $^1J_{\text{CP}} = 12.3\text{ Hz}$, CH_2), 129.01 (d, $^3J_{\text{CP}} = 10.4\text{ Hz}$, Ph, CH), 130.56 (d, $^4J_{\text{CP}} = 2.1\text{ Hz}$, Ph, para), 131.46 (d, $^2J_{\text{CP}} = 13.2\text{ Hz}$, Ph, CH), 134.02 (d, $^1J_{\text{CP}} = 30.0\text{ Hz}$, Ph, ipso), 195.76 (d, $^2J_{\text{CP}} = 8.2\text{ Hz}$, cis CO), 197.97 (d, $^2J_{\text{CP}} = 30.6\text{ Hz}$, trans CO). HRMS: m/z 459.9699 (calcd for $\text{C}_{13}\text{H}_9\text{O}_5\text{PW}$ 459.9697).

Synthesis of **15**: General Procedure A (24 h). White solids obtained with a yield of 17 %.

General Procedure B (12 h, yield 9%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -200.2 ($^1J_{\text{PW}} = 266$ Hz). ^1H NMR (CD_2Cl_2): δ 1.52 (m, 2H, CH_2), 1.84 (m, 2H, CH_2), 7.13 (ddd, $J = 4.9, 3.6, 1.2$ Hz, 1H, Th), 7.38 (ddd, $J = 8.4, 3.6, 1.0$ Hz, 1H, Th), 7.57 (ddd, $J = 4.9, 2.4, 1.0$ Hz, 1H, Th). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 13.69 (d, $^1J_{\text{CP}} = 11.2$ Hz, CH_2), 128.86 (d, $^3J_{\text{CP}} = 11.7$ Hz, Th, CH), 131.60 (d, $^4J_{\text{CP}} = 2.2$ Hz, Th, CH), 135.53 (d, $^1J_{\text{CP}} = 24.3$ Hz, Th, CH), 136.09 (d, $^2J_{\text{CP}} = 14.3$ Hz, Th, CH), 195.96 (d, $^2J_{\text{CP}} = 8.5$ Hz, cis CO), 198.16 (d, $^2J_{\text{CP}} = 31.9$ Hz, trans CO). HRMS: m/z 465.9261 (calcd for $\text{C}_{11}\text{H}_7\text{O}_5\text{PSW}$ 465.9261).

Synthesis of **16**: General Procedure A (3 h). White solids obtained with a yield of 26 %.

General Procedure B (12 h, yield 14%). ^{31}P NMR (CD_2Cl_2): δ -56.0 ($^1J_{\text{PW}} = 241$ Hz, $^1J_{\text{PH}} = 361.4$ Hz). ^1H NMR (CD_2Cl_2): δ 7.20 (ddd, $J = 4.8, 3.7, 1.1$ Hz, 2H, Th), 7.39 (d, $^1J_{\text{PH}} = 361.4$ Hz, 1H, PH), 7.49 (dd, $J = 7.7, 3.5$ Hz, 2H, Th), 7.70 (ddd, $J = 4.9, 2.6, 1.0$ Hz, 2H, Th). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 129.01 (d, $^3J_{\text{CP}} = 10.9$ Hz, Th, CH), 133.42 (d, $^4J_{\text{CP}} = 3.1$ Hz, Th, CH), 133.57 (d, $^1J_{\text{CP}} = 44.9$ Hz, Th, ipso), 136.37 (d, $^2J_{\text{CP}} = 12.2$ Hz, Th, CH), 196.38 (d, $^2J_{\text{CP}} = 6.9$ Hz, cis CO), 198.91 (d, $^2J_{\text{CP}} = 23.2$ Hz, trans CO). HRMS: m/z 521.8979 (calcd for $\text{C}_{13}\text{H}_7\text{O}_5\text{PS}_2\text{W}$ 521.8982).

Synthesis of **18**: General Procedure B (25 h, yield 4 %). General Procedure C (yield of 19 %).

White solids obtained. ^{31}P NMR (CD_2Cl_2): δ +12.8 ($^1J_{\text{PW}} = 253$ Hz, $^1J_{\text{PH}} = 366.9$ Hz). ^1H NMR (CD_2Cl_2): δ 4.69 (d, $^2J_{\text{PH}} = 22.3$ Hz, NH), 6.77-7.54 (m, 10H, Ph), 7.64 (d, $^1J_{\text{PH}} = 366.9$ Hz, PH). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 117.06 (d, $^3J_{\text{CP}} = 5.4$ Hz, PhN, ortho), 121.92 (s, PhN CH), 128.88 (d, $^2J_{\text{CP}} = 12.8$ Hz, Ph, ortho), 129.52 (d, $^3J_{\text{CP}} = 10.4$ Hz, Ph, meta), 129.70 (s, PhN CH), 131.00 (d, $^4J_{\text{CP}} = 1.4$ Hz, Ph, para), 135.80 (d, $^1J_{\text{CP}} = 50.2$ Hz, Ph, ipso), 143.99 (d, $^2J_{\text{CP}} = 11.0$ Hz, PhN, ipso), 196.26 (d, $^2J_{\text{CP}} = 7.1$ Hz, cis CO), 199.47 (d, $^2J_{\text{CP}} = 23.0$ Hz, trans CO). HRMS: m/z 524.9965 (calcd for $\text{C}_{17}\text{H}_{12}\text{NO}_5\text{PW}$ 524.9963).

Synthesis of **19**: General Procedure B (yield of 15% and 9 %). General Procedure C (yield of 6 %). ^{31}P NMR (CD_2Cl_2): δ +29.4 ($^1J_{\text{PW}} = 287$ Hz, $^1J_{\text{PH}} = 401.1$ Hz). ^1H NMR (CD_2Cl_2): δ 5.04 (dd, $^2J_{\text{PH}} = 14.2$ Hz, $^3J_{\text{HH}} = 6.6$ Hz, 2H, NH), 6.97-7.26 (m, 10H, Ph), 8.01 (dt, $^1J_{\text{PH}} = 401.1$ Hz, $^3J_{\text{HH}} = 6.6$ Hz, 1H, PH). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 119.39 (d, $^3J_{\text{CP}} = 6.0$ Hz, PhN, ortho), 123.05 (s, PhN CH), 129.78 (s, PhN CH), 143.16 (d, $^2J_{\text{CP}} = 5.8$ Hz, PhN, ipso), 196.09 (d, $^2J_{\text{CP}} = 7.7$ Hz, cis CO), 198.61 (d, $^2J_{\text{CP}} = 26.9$ Hz, trans CO). HRMS: m/z 540.0074 (calcd for $\text{C}_{17}\text{H}_{13}\text{N}_2\text{O}_5\text{PW}$ 540.0072).

Synthesis of **20**: General Procedure B (12 h). White solids obtained with a yield of 8 %. ^{31}P

NMR (CD_2Cl_2): δ -45.6 ($^1J_{\text{PW}} = 246$ Hz, $^1J_{\text{PH}} = 362.1$ Hz). ^1H NMR (CD_2Cl_2): δ 4.00 (d, $^2J_{\text{PH}} = 23.3$ Hz, 1H, NH), 6.60 (dt, $^1J_{\text{PH}} = 362.1$ Hz, $^3J_{\text{HH}} = 4.4$ Hz, 2H, PH), 6.96-7.34 (m, 5H, PhN). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 116.08 (d, $^3J_{\text{CP}} = 5.1$ Hz, PhN, ortho), 122.02 (s, PhN CH), 129.88 (s, PhN CH), 145.69 (d, $^2J_{\text{CP}} = 10.9$ Hz, PhN, ipso), 195.51 (d, $^2J_{\text{CP}} = 7.1$ Hz, cis CO), 198.32 (d, $^2J_{\text{CP}} = 24.1$ Hz, trans CO). HRMS: m/z 448.9651 (calcd for $\text{C}_{11}\text{H}_8\text{NO}_5\text{PW}$ 448.9650).

Synthesis of **21**: General Procedure A (17 h). Purification was performed via cold column chromatography (0 °C) with 20:1 hexane-dichloromethane. White solids obtained with a yield of 25% (for $\text{MeB}(\text{OH})_2$) and 21% (for $\text{EtB}(\text{OH})_2$). ^{31}P NMR (CD_2Cl_2): δ -86.9 ($^1J_{\text{PW}} = 221$ Hz, $^1J_{\text{PH}} = 342.6$ Hz). ^1H NMR (CD_2Cl_2): δ 5.80 (d, $^1J_{\text{PH}} = 342.6$ Hz, 2H, PH_2), 7.46-7.63 (m, 5H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 125.79 (d, $^1J_{\text{CP}} = 47.6$ Hz, Ph, ipso), 129.03 (d, $^3J_{\text{CP}} = 10.2$ Hz, Ph, CH), 131.10 (d, $^4J_{\text{CP}} = 2.3$ Hz, Ph, para), 133.28 (d, $^2J_{\text{CP}} = 11.5$ Hz, Ph, CH), 196.04 (d, $^2J_{\text{CP}} = 7.0$ Hz, cis CO), 199.02 (d, $^2J_{\text{CP}} = 22.2$ Hz, trans CO). HRMS: m/z 433.9543 (calcd for $\text{C}_{11}\text{H}_7\text{O}_5\text{PW}$ 433.9541).

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Chapter 3

Exploring the Applications of This New P-C Bond Synthesis

3.1 Introduction

With this new P-C bond synthesis involving the reaction of terminal phosphinidene complexes $[RP \rightarrow W(CO)_5]$ and arylboronic acids discovered, we were excited to expand the scope of this synthetic method and to find applications. An immediate question was whether this method could be extended to alkenylboronic acids. It is well-known that $[RP \rightarrow W(CO)_5]$ readily react with C=C bonds to form phosphirane complexes.^[1-2] We decided to find out if there is any competition between the cycloaddition and the P-C bond formation. Next, various attempts to apply this P-C bond to form other organophosphorus compounds were made.

3.2 Results and Discussion

We have checked that the potassium phosphate does not block the cycloaddition of terminal phosphinidene complex with alkene (Scheme 3.1).

Scheme 3.1 Reaction of **11a** with styrene in the presence and absence of K₃PO₄.

The reaction of **11** with alkenylboronic acids **26** in the absence of potassium phosphate was carried out in boiling toluene, phosphirane complexes **27** are obtained as mixtures of two isomeric products with isolated yields between 16 to 45% (Scheme 3.2).

Scheme 3.2 Reaction of **11** with alkenylboronic acids **26** without K₃PO₄.

Traces of water in the reaction media is responsible for the loss of the B(OH)₂ substituent during the course of the reaction. This was verified by NMR of the crude mixtures before chromatography. It is possible to obtain phosphiranylboronic acid **28** when extensively dried alkenylboronic acid **26a** was used (Scheme 3.3). Due to its limited stability, we were only able to characterise it from crude reaction mixture by ³¹P NMR and HRMS (calcd. mass for C₁₉H₁₄O₇PWB 580.0080; found 580.0081).

Scheme 3.3 Reaction of **11a** and **26a** under strict anhydrous condition.

When the reaction of **11** and alkenylboronic acids **26** was carried out in the presence of potassium phosphate, there was a dramatic change in the reaction pathway. Secondary alkenylphosphine complexes **29** are now the main products of the reaction (Scheme 3.4). Steric bulk in **26c** is the cause for the lower yields when compared to that for **26a**.

Scheme 3.4 Reaction of **11** with alkenylboronic acids **26** in the presence of K_3PO_4 .

We verified that there is no interconversion between phosphirane and alkenylphosphine complexes in the presence of potassium phosphate (Scheme 3.5). Thus, the alkenylphosphine complexes are formed as the primary products of the reaction.

Scheme 3.5 No interconversion between **27d** and **29b** in the presence of K_3PO_4 .

1-Alkenylphosphirane complexes **30** are formed when complex **11d** is used (Scheme 3.6). Despite the low yields of this synthesis, it is still a new addition to the limited number of reports on the syntheses of 1-alkenylphosphiranes.^[3-6]

Scheme 3.6 Formation of 1-alkenylphosphirane complexes **30** from the reaction of **11d** with alkenylboronic acids **26** in presence of K_3PO_4 .

We began our theoretical study to have a better understanding of this complete change in reaction pathway by firstly comparing the electronic structures of vinylboronic acid and its vinylborate adduct with the phosphate anion. Computations were carried out using DFT at the B3LYP/ 6-311+G(d,p) level.^[7] The occupied frontier orbitals of the two vinylboronic species are shown in Figure 3.1 to 3.3. The HOMO of vinylboronic acid is essentially the π C=C bond with a little contribution of the π lone pairs at oxygen, and the boron atom has a Mulliken charge of +0.47 (Figure 3.1). It is clear that the electrophilic terminal phosphinidene will selectively react with the vinyl group. The situation is totally different for the vinylborate adduct. In this case, the HOMO is solely localised on the terminal oxygen atoms of the phosphate (Figure 3.2), and a significant contribution of the borate oxygen lone pairs only appears in the HOMO-1 (Figure 3.3).

Figure 3.1 HOMO (Kohn-Sham) of vinylboronic acid.

Figure 3.2 HOMO (Kohn-Sham) of vinylborate adduct $[\text{CH}_2=\text{CH}-\text{B}(\text{OH})_2(\text{PO}_4)]^{3-}$.

Figure 3.3 HOMO-1 (Kohn-Sham) of vinylborate adduct $[\text{CH}_2=\text{CH}-\text{B}(\text{OH})_2(\text{PO}_4)]^{3-}$.

The electrophilic phosphinidene will tend to react with the terminal oxygen atoms of the borate adduct due to both steric and electronic factors. The theoretical investigation up to this point led to adduct **31** whose computed structure is shown in Figure 3.4. The phosphinidene phosphorus is still electrophilic in **31** (Mulliken charge +0.64) despite it bears a formal negative charge. The negative charge is delocalised onto the $W(CO)_5$ group. Since the vinylic carbon bonded to boron bears a negative charge of -0.12 , the intramolecular transfer of the vinyl group from boron to phosphorus in **31** appears to be favourable. The tentative proposed mechanism for the formation of secondary alkenylphosphine complexes is illustrated in Scheme 3.7.

Figure 3.4 Computed structure of adduct **31**. Main distances (Å) and angles (deg.): P15-W 2.898, P15-O13 1.649, O13-P11 1.737, P11-O9 1.605, O9-B10 1.550, B10-C4 1.642, C4---P15 5.110; W-P15-C28 103.38, W-P15-O13 111.80, O13-P15-C28 103.81.

Scheme 3.7 Proposed mechanism for the formation of secondary alkenylphosphine complex.

A similar mechanism could also operate simultaneously with the previously proposed B-O insertion mechanism in the arylation of phosphinidenes by arylboronic acids in the presence of potassium phosphate.

The following section contains our unpublished works and preliminary results. The reaction of **11f** with aryl- and alkenylboronic acids is shown in Scheme 3.8. The results show that alkenylboronic acid is incompatible with vinylphosphinidene complex and dialkenylphosphine complex cannot be synthesised via our method. The structure of complex **32c** is further confirmed by X-ray crystallography (Figure 3.3).

Scheme 3.8 Reaction of vinylphosphanorbornadiene complex **11f** with boronic acids in presence of K_3PO_4 .

Figure 3.5 X-ray crystal structure of **32c**. Main bond lengths (Å) and angles (deg): P-W 2.511(4), P-C4 1.796(12), P-C8 1.804(14); C4-P-W 117.6(4), C8-P-W 116.3(5), C4-P-C8 101.8(6).

Allylic phosphinidene complex is compatible with both aryl and alkenylboronic acids (Scheme 3.9). The low yields are partially due to the formation of side products from the dimerisation of allylic phosphinidene complex.

Scheme 3.9 Reactions of allylic phosphanorbornadiene complex **11g** with boronic acids in presence of K_3PO_4 .

A literature survey shows that a limited number of η^3 -1-phosphaallyl metal complexes were reported (Figure 3.6).^[8-15]

Figure 3.6 Types of η^3 -1-phosphaallyl metal complexes.

It would be interesting to use the secondary alkenylphosphine complexes formed via our method to generate phosphaallyl complexes. Complex **29a** was deprotonated with NaH and the metal complexes were added. The reactions involving $\text{Pd}(\text{OAc})_2$ and $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ show weak and messy ^{31}P NMR signals, while hydrolysis occurred in the case of $[\text{Ir}(\text{COD})\text{Cl}]_2$ and $\text{Rh}(\text{acac})(\text{CO})_2$. Attempts to synthesise new η^3 -1-phosphaallyl metal complex were unsuccessful.

Secondary alkenylphosphines can be converted into phosphaalkenes via base catalysis and heating.^[16-17] The possibility of generating phosphaalkene complexes from **29** was investigated. There was no conversion of complex **29** to phosphaalkene complex under similar reaction conditions. Next, the idea of generating phosphadiene complex from the deprotonation of secondary 2-chloromethylvinylphosphine complex was investigated (Scheme 3.10).

Scheme 3.10 Proposed idea of synthesis and trapping of phosphadiene complex.

Unfortunately, the reaction of **11a** with *trans*-2-chloromethylvinylboronic acid does not form the anticipated 2-chloromethylvinylphosphine complex (Scheme 3.11).

Scheme 3.11 Attempted reaction of **11a** with *trans*-2-chloromethylvinylboronic acid in presence of K₃PO₄.

Since the formation of phosphalkene complex from secondary alkenylphosphine complex was unsuccessful, we varied the phosphinidene substituents in hope to find a way to generate phosphalkene. The reactions of CH₂Cl and CO₂Et substituted phosphinidene complexes with phenylboronic acids in presence of phosphate simply lead to decomposition. The reaction works well with CH₂CO₂Et and CH₂CH₂CO₂Et substituted phosphinidene complexes (Scheme 3.12).

Scheme 3.12 Reaction of ester-containing phosphanorbornadiene complexes with phenylboronic acid in presence of K₃PO₄.

It appears that the reaction does not work when the phosphinidene complex bearing a reactive group on the α-carbon is used. This could be due to the interaction of this reactive group with the close boron atom in the proposed transient reaction intermediate which

leads to decomposition (Scheme 3.13). Trapping reagents (acetylenes and dienes) are inefficient as phosphinidene complexes are much more reactive to them than boronic acids.

Scheme 3.13 Proposed decomposition pathway based on B-O insertion product of phosphinidene complex.

Attempts to convert **34b** into phosphorus analogue of β -lactam via base-induced cyclisation with NaH and *t*-BuOK were unsuccessful (Scheme 3.14).

Scheme 3.14 Attempted synthesis of phosphorus analogue of β -lactam.

Lastly, we looked at ways to use this P-C bond synthesis to form phosphete and phosphetane. Alkenylphosphine complex **29a** was converted into complex **35**, and attempt to form phosphete via Lewis acid-induced cyclisation failed (Scheme 3.15) and complex **36** was obtained instead. Similar reaction was performed using **29c**, but its analogue of **35** decomposed during cold column chromatography.

Scheme 3.15 Attempted synthesis of phosphete complex from alkenylphosphine complex.

Reaction of phosphanorbornadiene complex **11j** with various boronic acids is summarised in Scheme 3.16. Reaction with phenylboronic acid gives secondary phosphine complex **37a** and phosphetane complex **38a** with isolated yields of 38% and 14% respectively. Reactions involving furyl- and thienylboronic acids give solely secondary phosphine complexes, while that of *trans*-2-phenylvinylboronic acid gives phosphetane complex with isolated yield of 23%.

Scheme 3.16 Reaction of **11j** with boronic acids in presence of K_3PO_4 .

Deprotonation of **37b** and **c** gives phosphetane complex **39a** and **b** respectively (Scheme 3.17). Structure of **39a** was further confirmed by X-ray crystallography (Figure 3.7).

Scheme 3.17 Formation of phosphetane complexes **39**.

These syntheses could serve as an additional method to the existing methods of phosphetane synthesis.^[18-20]

Figure 3.7 X-ray crystal structure of **39a**. Main bond lengths (Å) and angles (deg): P-W 2.5001(13), P-C4 1.795(6), P-C8 1.849(4), C8-C9 1.535(7); C4-P-W 116.9(3), C8-P-W 120.88(14), C8-P-C8A 78.0(3), C4-P-C8 106.8(2).

3.3 Conclusion

The reaction of terminal phosphinidene complexes $[RP \rightarrow W(CO)_5]$ with alkenylboronic acids is very sensitive to the presence and absence of solid potassium phosphate. The reaction products are phosphirane complexes without the salt and secondary alkenylphosphine complexes in the presence of the salt. This shift of reaction pathway can be explained by the formation of vinyborates in the presence of potassium phosphate. Many attempts to utilise this P-C bond synthesis to obtain other organophosphorus compounds were made, and 1-alkenylphosphirane and phosphetane complexes can be synthesised via this method.

3.4 Experimental

All reactions were performed under nitrogen using solvents dried by standard methods. NMR spectra were obtained using Bruker AV400 spectrometer operating at 400 MHz for 1H , 100.64 MHz for ^{13}C , 162.02 MHz for ^{31}P . Spectra were recorded at 298 K in either CD_2Cl_2 or C_6D_6 . All coupling constants (J values) are reported in Hertz (Hz). HRMS spectra were obtained on a Water Q-ToF Premier MS. Silica gel (230–400 mesh) was used for the chromatographic separations. Phosphanorbornadiene complexes were prepared based on literature.^[3, 21-25] Commercially available alkenylboronic acids were dried with the Dean-Stark technique prior to use.

General synthesis of phosphirane complex 27

A toluene mixture (2 mL) of phosphanorbornadiene complex **11** (0.3 mmol.) and alkenyl boronic acid **26** (0.9 mmol.) in a sealed tube was heated at 110 °C for 18h under inert

atmosphere. Solvent was evaporated and the residue was strained onto silica. Purification was performed via cold column chromatography at 0 °C with hexane.

General synthesis of secondary phosphine complexes **29**, **32-34** and **37**

A toluene mixture (3 mL) of phosphanorbornadiene complex **11** (0.3 mmol.), boronic acid (0.9 mmol.) and anhydrous K₃PO₄ (1.2 mmol.) in a sealed tube was heated at 110 °C for 18h under inert atmosphere. Solvent was evaporated and the residue was strained onto silica. Purification was performed via cold column chromatography at 0 °C with 15:1 hexane-dichloromethane (15: hexane-ethyl acetate for **34**).

27a^[26] Pale yellow solid (total yield 17 %). ³¹P{¹H} NMR (CD₂Cl₂): δ -149.0 (¹J_{PW} = 263 Hz; minor isomer) & -154.6 (¹J_{PW} = 259 Hz; major isomer). HRMS: m/z 536.0005 (calcd for C₁₉H₁₃O₅PW 536.0010).

27b White solid (total yield 26 %). HRMS: m/z 473.9857 (calcd for C₁₄H₁₁O₅PW 473.9854).

Isomer A ³¹P{¹H} NMR (CD₂Cl₂): δ -175.8 (¹J_{PW} = 254 Hz). ¹H NMR (CD₂Cl₂): δ 1.04 (d, ²J_{PH} = 7.0 Hz, 3H, Me), 1.66 (m, 1H, CH₂), 1.84 (m, 1H, CH₂), 2.94 (m, 1H, CH), 7.24-7.38 (m, 5H, Ph). ¹³C{¹H} NMR (CD₂Cl₂): δ 11.69 (d, ¹J_{CP} = 15.1 Hz, Me), 13.69 (d, ¹J_{CP} = 10.0 Hz, CH₂), 27.95 (d, ¹J_{CP} = 14.3 Hz, CH), 127.27 (d, ¹J_{CP} = 1.8 Hz, Ph), 129.07 (d, ¹J_{CP} = 4.1 Hz, Ph), 129.10 (d, ¹J_{CP} = 1.7

Hz, Ph), 135.50 (d, $^2J_{CP}$ = 5.7 Hz, ipso Ph), 196.25 (d, $^2J_{CP}$ = 8.4 Hz, cis CO), 198.76 (d, $^2J_{CP}$ = 29.8 Hz, trans CO).

Isomer B $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -162.6 ($^1J_{PW}$ = 262 Hz). ^1H NMR (CD_2Cl_2): δ 1.59 (d, $^2J_{PH}$ = 7.1 Hz, 3H, Me), 1.73 (m, 1H, CH_2), 1.83 (m, 1H, CH_2), 2.90 (m, 1H, CH), 7.21-7.32 (m, 5H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 14.38 (d, $^1J_{CP}$ = 12.6 Hz, CH_2), 19.13 (d, $^1J_{CP}$ = 13.9 Hz, Me), 27.96 (d, $^1J_{CP}$ = 14.7 Hz, CH), 127.31 (d, J_{CP} = 2.8 Hz, Ph), 128.64 (d, J_{CP} = 4.8 Hz, Ph), 129.01 (d, J_{CP} = 2.2 Hz, Ph), 137.74 (d, $^2J_{CP}$ = 1.3 Hz, ipso Ph), 195.61 (d, $^2J_{CP}$ = 8.4 Hz, cis CO), 198.23 (d, $^2J_{CP}$ = 30.8 Hz, trans CO).

27c Pale yellow solid (total yield 25 %). HRMS: m/z 550.0160 (calcd for $\text{C}_{20}\text{H}_{15}\text{O}_5\text{PW}$ 550.0167).

Isomer A $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -148.8 ($^1J_{PW}$ = 264 Hz). ^1H NMR (CD_2Cl_2): δ 1.72 (m, 1H, CH_2), 1.84 (m, 1H, CH_2), 2.87 (m, 1H, CH), 3.19 (d, $^2J_{PH}$ = 5.8 Hz, 2H, PBn CH_2), 7.19-7.40 (m, 10H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 12.76 (d, $^1J_{CP}$ = 14.4 Hz, CH_2), 26.65 (d, $^1J_{CP}$ = 16.8 Hz, CH), 39.65 (d, $^1J_{CP}$ = 7.4 Hz, Bn CH_2), 127.40 (d, J_{CP} = 2.4 Hz, Ph), 127.82 (d, J_{CP} = 3.0 Hz, Ph), 128.79 (d, J_{CP} = 4.7 Hz, Ph), 129.04 (d, J_{CP} = 1.8 Hz, Ph), 129.46 (d, J_{CP} = 2.2 Hz, Ph), 129.91 (d, J_{CP} = 5.3 Hz, Ph), 134.97 (d, $^2J_{CP}$ = 6.0 Hz, ipso Ph), 137.30 (s, ipso Ph), 195.40 (d, $^2J_{CP}$ = 8.2 Hz, cis CO), 197.80 (d, $^2J_{CP}$ = 32.3 Hz, trans CO).

Isomer B $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -157.5 ($^1J_{PW}$ = 256 Hz). ^1H NMR (CD_2Cl_2): δ 1.18 (m, 1H, CH_2), 2.12 (m, 1H, CH_2), 2.62 (m, 2H, PBn CH_2), 3.10 (m, 1H, CH), 6.89-7.43 (m, 10H, Ph). $^{13}\text{C}\{^1\text{H}\}$

NMR (CD₂Cl₂): δ 13.53 (d, $^1J_{CP}$ = 11.4 Hz, CH₂), 30.49 (d, $^1J_{CP}$ = 17.2 Hz, CH), 32.65 (d, $^1J_{CP}$ = 8.9 Hz, Bn CH₂), 127.54 (d, J_{CP} = 1.5 Hz, Ph), 127.59 (d, J_{CP} = 3.5 Hz, Ph), 128.98 (d, J_{CP} = 3.0 Hz, Ph), 129.32 (d, J_{CP} = 1.6 Hz, Ph), 129.35 (d, J_{CP} = 2.9 Hz, Ph), 129.94 (d, J_{CP} = 6.7 Hz, Ph), 135.14 (s, ipso Ph), 135.58 (d, $^2J_{CP}$ = 5.7 Hz, ipso Ph), 195.93 (d, $^2J_{CP}$ = 8.3 Hz, cis CO), 198.26 (d, $^2J_{CP}$ = 31.6 Hz, trans CO).

27d Pale yellow solid (total yield 45 %). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD₂Cl₂): δ -167.9 ($^1J_{PW}$ = 252 Hz; minor isomer) & -165.8 ($^1J_{PW}$ = 256 Hz; major isomer). ^1H NMR (CD₂Cl₂): δ 1.08-1.99 (m, 6H, alkyl), 7.38-7.53 (m, 5H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD₂Cl₂): δ 15.96 (d, $^2J_{CP}$ = 4.5 Hz, Me; minor isomer), 16.70 (d, $^1J_{CP}$ = 11.4 Hz, CH₂; minor isomer), 18.04 (d, $^2J_{CP}$ = 2.7 Hz, Me; major isomer), 18.99 (d, $^1J_{CP}$ = 13.6 Hz, CH₂; major isomer), 20.03 (d, $^1J_{CP}$ = 12.7 Hz, CH; major isomer), 20.37 (d, $^1J_{CP}$ = 14.1 Hz, CH; minor isomer), 129.13 (d, J_{CP} = 10.1 Hz, Ph), 130.50 (d, J_{CP} = 2.1 Hz, Ph; major isomer), 130.69 (d, J_{CP} = 1.9 Hz, Ph; minor isomer), 131.93 (d, J_{CP} = 12.2 Hz, Ph), 131.94 (d, $^1J_{CP}$ = 28.4 Hz, ipso Ph), 133.35 (d, J_{CP} = 11.7 Hz, Ph), 136.24 (d, $^1J_{CP}$ = 30.6 Hz, ipso Ph), 196.24 (d, $^2J_{CP}$ = 8.3 Hz, cis CO), 196.40 (d, $^2J_{CP}$ = 8.4 Hz, cis CO; minor isomer), 198.46 (d, $^2J_{CP}$ = 29.2 Hz, trans CO), 199.08 (d, $^2J_{CP}$ = 29.6 Hz, trans CO; minor isomer). HRMS: m/z 473.9846 (calcd for C₁₄H₁₁O₅PW 473.9854).

27e Pale yellow solid (total yield 21 %). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD₂Cl₂): δ -180.5 ($^1J_{PW}$ = 254 Hz). ^1H NMR (CD₂Cl₂): δ 1.25 (m, 3H, Me), 1.37 (d, $^2J_{PH}$ = 7.4 Hz, 3H, PMe), 1.41-1.53 (m, 3H, CH₂CH).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 17.06 (d, $^1J_{\text{CP}} = 12.0$ Hz, CH_2), 17.55 (d, $^1J_{\text{CP}} = 16.5$ Hz, PMe), 17.88 (d, $^1J_{\text{CP}} = 10.6$ Hz, CH), 17.98 (d, $^2J_{\text{CP}} = 2.8$ Hz, Me), 196.24 (d, $^2J_{\text{CP}} = 8.5$ Hz, cis CO), 198.60 (d, $^2J_{\text{CP}} = 28.7$ Hz, trans CO). HRMS: m/z 411.9686 (calcd for $\text{C}_9\text{H}_9\text{O}_5\text{PW}$ 411.9697).

27f White solid (total yield 23 %). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -165.6 ($^1J_{\text{PW}} = 256$ Hz). ^1H NMR (CD_2Cl_2): δ 0.80 (m, 1H, CH), 1.26 (m, 3H, Me), 1.49 (m, 2H, CH_2), 2.98 (m, 2H, Bn CH_2), 7.15-7.35 (m, 5H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 15.66 (d, $^1J_{\text{CP}} = 13.3$ Hz, PCH_2), 16.56 (d, $^1J_{\text{CP}} = 12.6$ Hz, PCH), 17.76 (d, $^2J_{\text{CP}} = 2.4$ Hz, Me), 38.38 (d, $^1J_{\text{CP}} = 10.0$ Hz, PCH_2Ph), 127.60 (d, $J_{\text{CP}} = 3.0$ Hz, Ph), 129.26 (d, $J_{\text{CP}} = 2.2$ Hz, Ph), 129.85 (d, $J_{\text{CP}} = 5.4$ Hz, Ph), 135.21 (d, $^2J_{\text{CP}} = 6.0$ Hz, ipso Ph), 196.05 (d, $^2J_{\text{CP}} = 8.3$ Hz, cis CO), 198.15 (d, $^2J_{\text{CP}} = 30.1$ Hz, trans CO). HRMS: m/z 488.0004 (calcd for $\text{C}_{15}\text{H}_{13}\text{O}_5\text{PW}$ 488.0010).

27g White solid (total yield 16 %). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -179.4 ($^1J_{\text{PW}} = 254$ Hz; minor isomer) & -175.4 ($^1J_{\text{PW}} = 256$ Hz; major isomer). ^1H NMR (CD_2Cl_2): δ 0.86-1.66 (m, 6H, alkyl), 1.93-2.11 (m, 2H, $\text{CH}_2\text{CH}_2\text{Cl}$), 3.64-3.80 (m, 2H, $\text{CH}_2\text{CH}_2\text{Cl}$). *Minor isomer* $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 15.08 (d, $^2J_{\text{CP}} = 4.2$ Hz, Me), 16.62 (d, $^1J_{\text{CP}} = 10.8$ Hz, CH_2), 18.86 (d, $^1J_{\text{CP}} = 13.0$ Hz, CH), 29.36 (d, $^1J_{\text{CP}} = 10.3$ Hz, $\text{PCH}_2\text{CH}_2\text{Cl}$), 41.57 (d, $^2J_{\text{CP}} = 6.8$ Hz, $\text{PCH}_2\text{CH}_2\text{Cl}$), 196.04 (d, $^2J_{\text{CP}} = 8.2$ Hz, cis CO), 198.11 (d, $^2J_{\text{CP}} = 29.5$ Hz, trans CO). *Major isomer* $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 16.98 (d, $^1J_{\text{CP}} = 13.3$ Hz, CH_2), 17.70 (d, $^2J_{\text{CP}} = 2.3$ Hz, Me), 17.93 (d, $^1J_{\text{CP}} = 11.7$ Hz, CH), 36.15 (d, $^1J_{\text{CP}} = 13.0$ Hz, $\text{PCH}_2\text{CH}_2\text{Cl}$), 41.52 (d, $^2J_{\text{CP}} = 3.8$ Hz, $\text{PCH}_2\text{CH}_2\text{Cl}$), 195.84 (d, $^2J_{\text{CP}} = 8.0$ Hz, cis

CO), 197.65 (d, $^2J_{CP} = 29.7$ Hz, trans CO). HRMS: m/z 459.9465 (calcd for $C_{10}H_{10}O_5PClW$ 459.9464).

29a Pale yellow solid (yield 50 %). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ -25.7 ($^1J_{PW} = 227$ Hz). 1H NMR (CD_2Cl_2): δ 6.60 (dd, $^1J_{PH} = 348.8$ Hz, $^3J_{HH} = 5.5$ Hz, 1H, PH), 6.73 (m, 1H, $PCH=$), 7.03-7.21 (m, 1H, $PhCH=$), 7.35-7.65 (m, 10H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 119.68 (d, $^1J_{CP} = 42.6$ Hz, $PCH=$), 127.80 (s, Ph), 129.29 (s, Ph), 129.53 (d, $J_{CP} = 10.0$ Hz, Ph), 130.13 (s, Ph), 130.95 (d, $J_{CP} = 1.6$ Hz, Ph), 132.23 (d, $^1J_{CP} = 46.4$ Hz, ipso Ph), 132.31 (d, $J_{CP} = 11.5$ Hz, Ph), 135.81 (d, $^3J_{CP} = 16.1$ Hz, ipso Ph), 146.43 (d, $^2J_{CP} = 7.7$ Hz, $=CHPh$), 196.74 (d, $^2J_{CP} = 6.9$ Hz, cis CO), 199.75 (d, $^2J_{CP} = 21.4$ Hz, trans CO). HRMS: m/z 536.0009 (calcd for $C_{19}H_{13}O_5PW$ 536.0010).

29b Pale yellow solid (yield 30 %). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ -28.4 ($^1J_{PW} = 226$ Hz). 1H NMR (CD_2Cl_2): δ 1.98 (m, 3H, Me), 6.07 (m, 1H, $PCH=$), 6.35 (dd, $^1J_{PH} = 347.2$ Hz, $^3J_{HH} = 5.2$ Hz, , 1H, PH), 6.41 (m, 1H, $=CHMe$), 7.44-7.56 (m, 5H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 20.42 (d, $^3J_{CP} = 16.2$ Hz, Me), 122.14 (d, $^1J_{CP} = 43.3$ Hz, $PCH=$), 129.38 (d, $J_{CP} = 10.0$ Hz, Ph), 130.66 (d, $^4J_{CP} = 2.1$ Hz, meta Ph), 132.00 (d, $J_{CP} = 11.4$ Hz, Ph), 132.91 (d, $^1J_{CP} = 46.5$ Hz, ipso Ph), 146.57 (d, $^2J_{CP} = 6.5$ Hz, $=CHMe$), 196.82 (d, $^2J_{CP} = 7.0$ Hz, cis CO), 199.96 (d, $^2J_{CP} = 20.6$ Hz, trans CO). HRMS: m/z 473.9840 (calcd for $C_{14}H_{11}O_5PW$ 473.9854).

29c Pale yellow solid (yield 21 %). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -12.3 ($^1J_{\text{PW}} = 231$ Hz). ^1H NMR (CD_2Cl_2): δ 5.94 (d, $^3J_{\text{PH}} = 18.9$ Hz, 1H, =CH₂), 6.07 (d, $^3J_{\text{PH}} = 37.9$ Hz, 1H, =CH₂), 6.76 (d, $^1J_{\text{PH}} = 345.4$ Hz, 1H, PH), 7.18-7.66 (m, 10H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 127.71 (d, $J_{\text{CP}} = 4.1$ Hz, Ph), 128.91 (s, Ph), 128.97 (s, Ph), 129.48 (d, $J_{\text{CP}} = 9.9$ Hz, Ph), 129.68 (d, $^2J_{\text{CP}} = 15.2$ Hz, =CH₂), 131.12 (d, $J_{\text{CP}} = 2.0$ Hz, Ph), 131.38 (d, $^1J_{\text{CP}} = 43.1$ Hz, ipso Ph), 133.05 (d, $J_{\text{CP}} = 11.2$ Hz, Ph), 139.56 (d, $^2J_{\text{CP}} = 7.6$ Hz, ipso Ph), 144.03 (d, $^1J_{\text{CP}} = 32.4$ Hz, PC=), 196.59 (d, $^2J_{\text{CP}} = 6.7$ Hz, cis CO), 199.48 (d, $^2J_{\text{CP}} = 22.0$ Hz, trans CO). HRMS: m/z 536.0016 (calcd for $\text{C}_{19}\text{H}_{13}\text{O}_5\text{PW}$ 536.0010).

29d Pale yellow solid (yield 36 %). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -55.5 ($^1J_{\text{PW}} = 226$ Hz). ^1H NMR (CD_2Cl_2): δ 1.90 (dd, $^2J_{\text{PH}} = 8.2$ Hz, $^3J_{\text{HH}} = 6.6$ Hz, 3H, Me), 5.69 (ddq, $^1J_{\text{PH}} = 343.5$ Hz, $^3J_{\text{HH}} = 6.3$ Hz, $^3J_{\text{HH}} = 6.2$ Hz, 1H, PH), 6.61 (ddd, $^2J_{\text{PH}} = 21.6$ Hz, $^3J_{\text{HH}} = 16.3$ Hz, $^3J_{\text{HH}} = 5.4$ Hz, 1H, PCH=), 7.06 (dd, $^3J_{\text{PH}} = 19.9$ Hz, $^3J_{\text{HH}} = 17.3$ Hz, , 1H, PhCH=), 7.33-7.50 (m, 5H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 13.26 (d, $^1J_{\text{CP}} = 31.0$ Hz, MeP), 120.74 (d, $^1J_{\text{CP}} = 43.6$ Hz, PCH=), 127.55 (s, Ph), 129.28 (s, Ph), 129.91 (s, Ph), 135.89 (d, $^3J_{\text{CP}} = 15.2$ Hz, ipso Ph), 144.08 (d, $^2J_{\text{CP}} = 5.2$ Hz, =CHPh), 196.83 (d, $^2J_{\text{CP}} = 7.0$ Hz, cis CO), 199.97 (d, $^2J_{\text{CP}} = 20.3$ Hz, trans CO). HRMS: m/z 473.9841 (calcd for $\text{C}_{14}\text{H}_{11}\text{O}_5\text{PW}$ 473.9854).

29e Pale yellow solid (yield 60 %). ^{31}P NMR $\{^1\text{H}\}$ (CD_2Cl_2): δ -26.2 ($^1J_{\text{PW}} = 227$ Hz). ^1H NMR (CD_2Cl_2): δ 3.44 (m, 2H, CH_2), 5.67 (pseudo dq, $^1J_{\text{PH}} = 342.4$ Hz, 1H, PH), 6.46 (ddd, $^2J_{\text{PH}} = 20.2$ Hz, $^3J_{\text{HH}} = 17.0$ Hz, $^3J_{\text{HH}} = 7.0$ Hz, 1H, PCH=), 6.93 (dd, $^3J_{\text{PH}} = 18.9$ Hz, $^3J_{\text{HH}} = 17.3$ Hz, , 1H, PhCH=), 7.28-7.43 (m, 10H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 37.17 (d, $^1J_{\text{CP}} = 23.8$ Hz, CH_2), 118.61 (d, $^1J_{\text{CP}} = 41.7$ Hz, PCH=), 127.50 (d, $J_{\text{CP}} = 2.9$ Hz, Ph), 127.58 (s, Ph), 129.25 (s, Ph), 129.27 (s, Ph), 129.55 (d, $J_{\text{CP}} = 4.7$ Hz, Ph), 129.99 (s, Ph), 135.89 (d, $^3J_{\text{CP}} = 14.7$ Hz, ipso Ph), 136.66 (d, $^2J_{\text{CP}} = 8.2$ Hz, ipso Ph), 146.31 (d, $^2J_{\text{CP}} = 5.1$ Hz, $=\text{CHPh}$), 196.63 (d, $^2J_{\text{CP}} = 6.9$ Hz, cis CO), 199.61 (d, $^2J_{\text{CP}} = 21.4$ Hz, trans CO). HRMS: m/z 550.0168 (calcd for $\text{C}_{20}\text{H}_{15}\text{O}_5\text{PW}$ 550.167).

29f Pale yellow solid (yield 25 %). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -29.0 ($^1J_{\text{PW}} = 227$ Hz). ^1H NMR (CD_2Cl_2): δ 1.88 (d, $^3J_{\text{HH}} = 6.0$, 3H, Me), 3.31 (m, 2H, CH_2), 5.43 (pseudo dq, $^1J_{\text{PH}} = 342.0$ Hz, 1H, PH), 5.79 (m, 1H, PCH=), 6.16 (m, 1H, $=\text{CHMe}$), 7.26-7.35 (m, 5H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 20.38 (d, $^3J_{\text{CP}} = 15.1$ Hz, Me), 37.03 (d, $^1J_{\text{CP}} = 24.1$ Hz, CH_2), 120.82 (d, $^1J_{\text{CP}} = 42.2$ Hz, PCH=), 127.34 (d, $J_{\text{CP}} = 2.8$ Hz, Ph), 129.13 (d, $J_{\text{CP}} = 2.3$ Hz, Ph), 129.55 (d, $J_{\text{CP}} = 4.7$ Hz, Ph), 136.84 (d, $^2J_{\text{CP}} = 8.1$ Hz, ipso Ph), 146.20 (d, $^2J_{\text{CP}} = 4.0$ Hz, $=\text{CHMe}$), 196.72 (d, $^2J_{\text{CP}} = 7.0$ Hz, cis CO), 199.80 (d, $^2J_{\text{CP}} = 21.0$ Hz, trans CO). HRMS: m/z 487.9999 (calcd for $\text{C}_{15}\text{H}_{13}\text{O}_5\text{PW}$ 488.0010).

29g Pale yellow solid (yield 19 %). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -15.3 ($^1J_{\text{PW}} = 228$ Hz). ^1H NMR (CD_2Cl_2): δ 3.52 (m, 2H, CH_2), 5.75 (d, $^3J_{\text{PH}} = 17.3$ Hz, 1H, $=\text{CH}_2$), 5.87 (pseudo dt, $^1J_{\text{PH}} = 343.0$ Hz, 1H, PH), 5.96 (dd, $^3J_{\text{PH}} = 35.0$ Hz, $J_{\text{HH}} = 1.0$ Hz, 1H, $=\text{CH}_2$), 7.20-7.43 (m, 10H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 36.34 (d, $^1J_{\text{CP}} = 21.1$ Hz, CH_2), 127.32 (d, $^2J_{\text{CP}} = 11.8$ Hz, $=\text{CH}_2$), 127.45 (d, $J_{\text{CP}} = 4.3$ Hz, Ph), 127.59 (d, $J_{\text{CP}} = 3.1$ Hz, Ph), 128.97 (s, Ph), 129.14 (s, Ph), 129.26 (d, $J_{\text{CP}} = 2.3$ Hz, Ph), 129.59 (d, $J_{\text{CP}} = 4.9$ Hz, Ph), 136.27 (d, $^2J_{\text{CP}} = 6.9$ Hz, ipso Ph), 139.84 (d, $^2J_{\text{CP}} = 8.0$ Hz, ipso Ph), 143.71 (d, $^1J_{\text{CP}} = 31.6$ Hz, $\text{PC}=\text{CH}_2$), 196.51 (d, $^2J_{\text{CP}} = 6.8$ Hz, cis CO), 199.44 (d, $^2J_{\text{CP}} = 22.7$ Hz, trans CO). HRMS: m/z 550.0159 (calcd for $\text{C}_{20}\text{H}_{15}\text{O}_5\text{PW}$ 550.0167).

29h Pale yellow solid (yield 15 %). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -44.4 ($^1J_{\text{PW}} = 229$ Hz). ^1H NMR (CD_2Cl_2): δ 2.55 (m, 2H, PCH_2), 3.77 (m, 2H, CH_2Cl), 5.79 (dm, $^1J_{\text{PH}} = 345.9$ Hz, 1H, PH), 6.50 (ddd, $^2J_{\text{PH}} = 22.9$ Hz, $^3J_{\text{HH}} = 17.0$ Hz, $^3J_{\text{HH}} = 7.8$ Hz, 1H, $\text{PCH}=\text{CH}_2$), 7.13 (dd, $^3J_{\text{PH}} = 19.5$ Hz, $^3J_{\text{HH}} = 17.2$ Hz, 1H, $\text{PhCH}=\text{CH}_2$), 7.37-7.50 (m, 5H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 33.04 (d, $^1J_{\text{CP}} = 24.7$ Hz, PCH_2), 42.09 (d, $^2J_{\text{CP}} = 4.7$ Hz, CH_2Cl), 117.29 (d, $^1J_{\text{CP}} = 42.9$ Hz, $\text{PCH}=\text{CH}_2$), 127.69 (s, Ph), 129.32 (s, Ph), 130.23 (s, Ph), 135.60 (d, $^3J_{\text{CP}} = 14.8$ Hz, ipso Ph), 146.18 (d, $^2J_{\text{CP}} = 3.3$ Hz, $=\text{CHPh}$), 196.38 (d, $^2J_{\text{CP}} = 7.0$ Hz, cis CO), 199.26 (d, $^2J_{\text{CP}} = 21.4$ Hz, trans CO). HRMS: m/z 521.9604 (calcd for $\text{C}_{15}\text{H}_{12}\text{O}_5\text{ClPW}$ 521.9620).

30a Pale yellow solid (yield 19 %). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -192.0 ($^1J_{\text{PW}} = 261$ Hz). ^1H NMR (CD_2Cl_2): δ 1.42 (m, 2H, CH_2), 1.64 (m, 2H, CH_2), 5.87 (dd, $^2J_{\text{PH}} = 9.4$ Hz, $^3J_{\text{HH}} = 17.0$ Hz, 1H, PCH=), 7.14 (dd, $^3J_{\text{PH}} = 23.7$ Hz, $^3J_{\text{HH}} = 17.0$ Hz, 1H, PhCH=), 7.31-7.42 (m, 5H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 11.04 (d, $^1J_{\text{CP}} = 10.2$ Hz, PCH_2), 125.08 (d, $^1J_{\text{CP}} = 29.7$ Hz, PCH=), 127.32 (s, Ph), 129.26 (s, Ph), 129.88 (s, Ph), 135.70 (d, $^3J_{\text{CP}} = 19.6$ Hz, ipso Ph), 148.10 (d, $^2J_{\text{CP}} = 18.2$ Hz, $=\text{CHPh}$), 196.08 (d, $^2J_{\text{CP}} = 8.4$ Hz, cis CO), 198.23 (d, $^2J_{\text{CP}} = 29.5$ Hz, trans CO). HRMS: m/z 485.9866 (calcd for $\text{C}_{15}\text{H}_{11}\text{O}_5\text{PW}$ 485.9854).

30b Pale yellow solid (yield 5 %). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -184.2 ($^1J_{\text{PW}} = 258$ Hz). ^1H NMR (CD_2Cl_2): δ 1.38 (m, 2H, CH_2), 1.66 (m, 2H, CH_2), 5.85 (d, $^3J_{\text{PH}} = 18.3$ Hz, 1H, $=\text{CH}_2$), 5.91 (d, $^3J_{\text{PH}} = 36.9$ Hz, 1H, $=\text{CH}_2$), 7.36-7.47 (m, 5H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 10.77 (d, $^1J_{\text{CP}} = 12.7$ Hz, CH_2), 126.50 (d, $^2J_{\text{CP}} = 11.8$ Hz, $=\text{CH}_2$), 127.86 (s, Ph), 127.91 (s, Ph), 129.10 (s, Ph), 137.82 (d, $^2J_{\text{CP}} = 10.9$ Hz, ipso Ph), 146.07 (d, $^1J_{\text{CP}} = 20.7$ Hz, PC=), 196.00 (d, $^2J_{\text{CP}} = 8.3$ Hz, cis CO), 198.41 (d, $^2J_{\text{CP}} = 30.1$ Hz, trans CO). HRMS: m/z 485.9856 (calcd for $\text{C}_{15}\text{H}_{11}\text{O}_5\text{PW}$ 485.9854).

Synthesis of **11f**. Procedure as stated in literature. Vinylmagnesium bromide used instead.^[27]

Yellow solid (20%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ +4.6 ($^1J_{\text{PW}} = 212$ Hz). ^1H NMR (CD_2Cl_2): δ 2.15 (s, 6H, Me), 5.93 (m, 3H, CH_2 & CH), 6.34 (d, $^2J_{\text{PH}} = 36.7$ Hz, 2H, PCH). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 17.46 (d, $^3J_{\text{CP}} = 11.5$ Hz, Me), 128.95 (d, $^1J_{\text{CP}} = 44.6$ Hz, PCH=), 130.53 (d, $^1J_{\text{CP}} = 36.4$ Hz, PCH=CH $_2$), 131.57 (d, $^2J_{\text{CP}} = 5.8$ Hz, PCH=CH $_2$), 152.06 (d, $^2J_{\text{CP}} = 8.7$ Hz, =CMe), 196.59 (d, $^2J_{\text{CP}} = 6.7$ Hz, cis CO), 199.73 (d, $^2J_{\text{CP}} = 17.9$ Hz, trans CO). HRMS: m/z 461.9877 (calcd for $\text{C}_{13}\text{H}_{11}\text{O}_5\text{PW}$ 461.9854).

11f Bright yellow solid (73%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ +205.6 ($^1J_{\text{PW}} = 237$ Hz). ^1H NMR (CD_2Cl_2): δ 2.00 (s, 6H, Me), 3.76 (d, $^2J_{\text{PH}} = 5.8$ Hz, 2H, PCH), 3.77 (s, 6H, Me), 5.58 (m, 1H, =CH $_2$), 5.84 (m, 1H, =CH $_2$), 6.38 (m, 1H, PCH=). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 16.00 (d, $^3J_{\text{CP}} = 2.5$ Hz, Me), 52.70 (s, Me), 60.03 (d, $^1J_{\text{CP}} = 21.9$ Hz, PCH), 129.31 (d, $^2J_{\text{CP}} = 1.1$ Hz, =CH $_2$), 138.53 (d, $^1J_{\text{CP}} = 6.3$ Hz, PCH=), 138.65 (d, $^2J_{\text{CP}} = 16.6$ Hz, =CMe), 146.36 (d, $^2J_{\text{CP}} = 4.7$ Hz, CCO $_2$ Me), 165.38 (d, $^3J_{\text{CP}} = 2.9$ Hz, CO $_2$ Me), 196.39 (d, $^2J_{\text{CP}} = 6.7$ Hz, cis CO), 198.81 (d, $^2J_{\text{CP}} = 25.1$ Hz, trans CO). HRMS: m/z 604.0091 (calcd for $\text{C}_{19}\text{H}_{17}\text{O}_9\text{PW}$ 604.0120).

32b White solid (16%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -24.5 ($^1J_{\text{PW}} = 226$ Hz). ^1H NMR (CD_2Cl_2): δ 5.81-6.06 (m, 2H, CH_2), 6.41 (dd, $^1J_{\text{PH}} = 348.2$ Hz, $^3J_{\text{HH}} = 5.3$ Hz, 1H, PH), 6.47 (m, 1H, PCH=), 7.46-7.60 (m, 5H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 129.52 (d, $J_{\text{CP}} = 10$ Hz, Ph), 130.82 (d, $^1J_{\text{CP}} = 38.1$ Hz, PCH=), 131.02 (d, $J_{\text{CP}} = 1.9$ Hz, Ph), 131.30 (d, $^1J_{\text{CP}} = 46.3$ Hz, ipso Ph), 132.25 (d, $^2J_{\text{CP}} = 3.1$ Hz, $=\text{CH}_2$), 132.49 (d, $J_{\text{CP}} = 11.2$ Hz, Ph), 196.59 (d, $^2J_{\text{CP}} = 6.9$ Hz, cis CO), 199.70 (d, $^2J_{\text{CP}} = 20.4$ Hz, trans CO). HRMS: m/z 459.9676 (calcd for $\text{C}_{13}\text{H}_9\text{O}_5\text{PW}$ 459.9697).

32c White solid (25%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -44.6 ($^1J_{\text{PW}} = 234$ Hz). ^1H NMR (CD_2Cl_2): δ 5.74-5.97 (m, 2H, CH_2), 6.44 (m, 1H, PCH=), 6.65 (dd, $^1J_{\text{PH}} = 355.7$ Hz, $^3J_{\text{HH}} = 6.1$ Hz, 1H, PH), 7.25 (m, 1H, Th), 7.50 (m, 1H, Th), 7.75 (m, 1H, Th). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 129.21 (d, $J_{\text{CP}} = 10.9$ Hz, Th), 130.12 (d, $^1J_{\text{CP}} = 43.8$ Hz, ipso Th), 130.45 (s, CH_2), 131.91 (d, $^1J_{\text{CP}} = 43.4$ Hz, PCH=), 133.72 (d, $J_{\text{CP}} = 2.7$ Hz, Th), 137.25 (d, $J_{\text{CP}} = 11.9$ Hz, Th), 196.41 (d, $^2J_{\text{CP}} = 6.9$ Hz, cis CO), 199.26 (d, $^2J_{\text{CP}} = 21.7$ Hz, trans CO). HRMS: m/z 465.9253 (calcd for $\text{C}_{11}\text{H}_7\text{O}_5\text{PSW}$ 465.9261).

33a Pale yellow solid (18%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -22.0 ($^1J_{\text{PW}} = 228$ Hz). ^1H NMR (CD_2Cl_2): δ 2.97 (m, 2H, PCH_2), 5.04-5.14 (m, 2H, $=\text{CH}_2$), 5.69 (m, 1H, $\text{CH}=\text{}$), 5.80 (dm, $^1J_{\text{PH}} = 342.0$ Hz, 1H, PH), 7.46-7.56 (m, 5H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 35.46 (d, $^1J_{\text{CP}} = 24.3$ Hz, PCH_2), 119.80 (d, $^3J_{\text{CP}} = 10.5$ Hz, $=\text{CH}_2$), 129.36 (d, $J_{\text{CP}} = 9.8$ Hz, Ph), 130.91 (d, $J_{\text{CP}} = 1.9$ Hz, Ph), 131.89 (d, $^1J_{\text{CP}} = 43.0$ Hz, ipso Ph), 132.06 (d, $^2J_{\text{CP}} = 8.5$ Hz, $\text{CH}=\text{}$), 132.32 (d, $J_{\text{CP}} = 10.2$ Hz, Ph), 196.73 (d, $^2J_{\text{CP}} = 6.9$ Hz, cis CO), 199.72 (d, $^2J_{\text{CP}} = 21.6$ Hz, trans CO). HRMS: m/z 473.9852 (calcd for $\text{C}_{14}\text{H}_{11}\text{O}_5\text{PW}$ 473.9854).

33b Pale yellow solid (8%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -35.1 ($^1J_{\text{PW}} = 228$ Hz). ^1H NMR (CD_2Cl_2): δ 2.91 (m, 2H, PCH_2), 5.21-5.27 (m, 2H, $=\text{CH}_2$), 5.57 (dm, $^1J_{\text{PH}} = 341.6$ Hz, 1H, PH), 5.86 (m, 1H, $\text{CH}=\text{CH}_2$), 6.55 (m, 1H, $\text{PCH}=\text{}$), 7.09 (m, 1H, $=\text{CHPh}$), 7.34-7.49 (m, 5H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 34.38 (d, $^1J_{\text{CP}} = 26.9$ Hz, PCH_2), 118.57 (d, $^1J_{\text{CP}} = 42.1$ Hz, $\text{PCH}=\text{}$), 119.96 (d, $^3J_{\text{CP}} = 10.4$ Hz, $=\text{CH}_2$), 127.63 (s, Ph), 129.28 (s, Ph), 130.00 (s, Ph), 132.26 (d, $^2J_{\text{CP}} = 8.3$ Hz, $\text{CH}=\text{CH}_2$), 135.87 (d, $^3J_{\text{CP}} = 15.1$ Hz, ipso Ph), 145.97 (d, $^2J_{\text{CP}} = 5.3$ Hz, $=\text{CHPh}$), 196.72 (d, $^2J_{\text{CP}} = 7.0$ Hz, cis CO), 199.67 (d, $^2J_{\text{CP}} = 22.3$ Hz, trans CO). HRMS: m/z 500.0004 (calcd for $\text{C}_{16}\text{H}_{13}\text{O}_5\text{PW}$ 500.0010).

Synthesis of **11h**. Procedure similar to literature; Ethyl chloroacetate used instead.^[25]

Yellow solid obtained (28%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -3.1 ($^1J_{\text{PW}} = 217$ Hz). ^1H NMR (CD_2Cl_2): δ 1.26 (t, $^3J_{\text{HH}} = 7.1$ Hz, 3H, CH_2CH_3), 2.16 (s, 6H, Me), 3.00 (d, $^2J_{\text{PH}} = 8.0$ Hz, 2H, CH_2), 4.14 (q, $^3J_{\text{HH}} = 7.1$ Hz, 2H, CH_2CH_3), 6.42 (d, $^2J_{\text{PH}} = 37.1$ Hz, 2H, $\text{PCH}=\text{}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 14.37 (s, CH_2CH_3), 7.38 (d, $^3J_{\text{CP}} = 11.8$ Hz, Me), 36.84 (d, $^1J_{\text{CP}} = 18.4$ Hz, PCH_2), 61.95 (s, CH_2O), 129.09 (d, $^1J_{\text{CP}} = 42.6$ Hz, $\text{PCH}=\text{}$), 151.95 (d, $^2J_{\text{CP}} = 9.2$ Hz, $=\text{CMe}$), 168.28 (d, $^2J_{\text{CP}} = 3.1$ Hz, CO_2), 196.25 (d, $^2J_{\text{CP}} = 6.9$ Hz, cis CO), 199.44 (d, $^2J_{\text{CP}} = 19.3$ Hz, trans CO). HRMS: m/z 522.0061 (calcd for $\text{C}_{15}\text{H}_{15}\text{O}_7\text{PW}$ 522.0065).

11h Bright yellow solid (80%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ +192.8 ($^1J_{\text{PW}} = 243$ Hz). ^1H NMR (CD_2Cl_2): δ 1.26 (t, $^3J_{\text{HH}} = 7.1$ Hz, 3H, CH_2CH_3), 1.99 (d, $^4J_{\text{PH}} = 1.4$ Hz, 6H, Me), 3.44 (d, $^2J_{\text{PH}} = 2.7$ Hz, 2H, PCH_2), 3.72 (d, $^2J_{\text{PH}} = 1.4$ Hz, 2H, PCH), 3.80 (s, 6H, OMe), 4.15 (t, $^3J_{\text{HH}} = 7.1$ Hz, 2H, CH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 14.20 (s, OCH_2CH_3), 16.10 (d, $^3J_{\text{CP}} = 1.9$ Hz, Me), 42.73 (d, $^1J_{\text{CP}} = 3.8$ Hz, PCH_2), 52.79 (s, OMe), 59.98 (d, $^1J_{\text{CP}} = 21.1$ Hz, PCH), 62.17 (s, OCH_2CH_3), 138.65 (d, $^2J_{\text{CP}} = 17.3$ Hz, $=\text{CMe}$), 145.60 (d, $^2J_{\text{CP}} = 4.8$ Hz, $=\text{CCO}_2$), 165.31 (d, $^3J_{\text{CP}} = 2.9$ Hz, $=\text{CCO}_2$), 168.05 (s, CO_2), 196.14 (d, $^2J_{\text{CP}} = 6.7$ Hz, cis CO), 198.08 (d, $^2J_{\text{CP}} = 26.9$ Hz, trans CO). HRMS: m/z 664.0330 (calcd for $\text{C}_{21}\text{H}_{21}\text{O}_{11}\text{PW}$ 664.0331).

34a White solid (15%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -31.5 ($^1J_{\text{PW}} = 234$ Hz). ^1H NMR (CD_2Cl_2): δ 1.09 (t, $^3J_{\text{HH}} = 7.1$ Hz, 3H, CH_2CH_3), 3.22 (m, 2H, PCH_2), 4.01 (m, 2H, CH_2CH_3), 6.25 (ddd, $^1J_{\text{PH}} = 354.1$ Hz, $^3J_{\text{HH}} = 7.9$ Hz, $^3J_{\text{HH}} = 5.6$ Hz, 1H, PH), 7.47-7.61 (m, 5H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 14.10 (s, OCH_2CH_3), 36.96 (d, $^1J_{\text{CP}} = 19.5$ Hz, PCH_2), 62.03 (s, OCH_2CH_3), 129.49 (d, $J_{\text{CP}} = 10.0$ Hz, Ph), 131.28 (d, $^1J_{\text{CP}} = 44.7$ Hz, ipso Ph), 131.38 (d, $J_{\text{CP}} = 1.9$ Hz, Ph), 132.22 (d, $J_{\text{CP}} = 11.2$ Hz, Ph), 168.61 (d, $^2J_{\text{CP}} = 6.0$ Hz, CO_2), 196.26 (d, $^2J_{\text{CP}} = 6.9$ Hz, cis CO), 199.22 (d, $^2J_{\text{CP}} = 22.9$ Hz, trans CO). HRMS: m/z 519.9928 (calcd for $\text{C}_{15}\text{H}_{13}\text{O}_7\text{PW}$ 519.9908).

34b White solid (18%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -24.6 ($^1J_{\text{PW}} = 226$ Hz). ^1H NMR (CD_2Cl_2): δ 1.21 (t, $^3J_{\text{HH}} = 7.1$ Hz, 3H, CH_2CH_3), 2.42 (m, 4H, CH_2), 4.08 (q, $^3J_{\text{HH}} = 7.1$ Hz, 2H, CH_2CH_3), 5.84 (ddd, $^1J_{\text{PH}} = 342.0$ Hz, $^3J_{\text{HH}} = 7.5$ Hz, $^3J_{\text{HH}} = 4.8$ Hz, 1H, PH), 7.47-7.57 (m, 5H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 14.34 (s, OCH_2CH_3), 25.77 (d, $^1J_{\text{CP}} = 25.7$ Hz, PCH_2CH_2), 32.43 (d, $^2J_{\text{CP}} = 4.8$ Hz, PCH_2CH_2), 61.37 (s, OCH_2), 129.59 (d, $J_{\text{CP}} = 9.8$ Hz, Ph), 131.08 (d, $J_{\text{CP}} = 2.0$ Hz, Ph), 131.42 (d, $^1J_{\text{CP}} = 43.9$ Hz, ipso Ph), 132.15 (d, $J_{\text{CP}} = 10.6$ Hz, Ph), 171.78 (d, $^3J_{\text{CP}} = 9.8$ Hz, CO_2), 196.59 (d, $^2J_{\text{CP}} = 7.0$ Hz, cis CO), 199.61 (d, $^2J_{\text{CP}} = 20.9$ Hz, trans CO). HRMS: m/z 534.0071 (calcd for $\text{C}_{16}\text{H}_{15}\text{O}_7\text{PW}$ 534.0065).

Synthesis of 35. Sodium hydride (24 mg, 1 mmol.) was added to 2 mL THF solution of **29a** (264 mg, 0.49 mmol.) at 0 °C and the reaction mixture was warmed to room temperature over 30 min. Paraformaldehyde (30 mg, 1 mmol.) was added at 0 °C and the reaction mixture was warmed to room temperature over 1h. EtOH (0.2 mL) was added and stirred for 30 min. Purification was performed via cold column chromatography at 0 °C with 10:1 hexane-ethyl acetate followed by 5:1 hexane-ethyl acetate. White solid (100 mg) was obtained with yield of 36 %.

$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ +7.8 ($^1J_{\text{PW}} = 234$ Hz). ^1H NMR (CD_2Cl_2): δ 2.07 (br s, 1H, OH), 4.51 (m, 2H, CH_2), 6.85 (dd, $^2J_{\text{PH}} = 12.5$ Hz, $^3J_{\text{HH}} = 17.2$ Hz, 1H, PCH=), 7.32 (dd, $^3J_{\text{PH}} = 17.6$ Hz, $^3J_{\text{HH}} = 17.6$ Hz, 1H, $=\text{CHPh}$), 7.38-7.65 (m, 10H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 66.36 (d, $^1J_{\text{CP}} = 29.9$ Hz, CH_2OH), 120.19 (d, $^1J_{\text{CP}} = 42.8$ Hz, PCH=), 127.86 (s, Ph), 129.33 (s, Ph), 129.47 (d, $J_{\text{CP}} = 9.4$ Hz, Ph), 130.24 (s, Ph), 130.77 (d, $J_{\text{CP}} = 2.0$ Hz, Ph), 131.51 (d, $J_{\text{CP}} = 10.2$ Hz, Ph), 133.51 (d, $^1J_{\text{CP}} = 41.8$ Hz, ipso Ph), 135.90 (d, $^3J_{\text{CP}} = 15.8$ Hz, ipso Ph), 148.29 (d, $^2J_{\text{CP}} = 10.5$ Hz, $=\text{CHPh}$), 196.97 (d, $^2J_{\text{CP}} = 6.9$ Hz, cis CO), 199.60 (d, $^2J_{\text{CP}} = 20.8$ Hz, trans CO). HRMS: m/z 566.0088 (calcd for $\text{C}_{20}\text{H}_{15}\text{O}_6\text{PW}$ 566.0116).

Synthesis of 36. 0.5 mL of 1M Boron trichloride solution in DCM was added to **35** (57 mg, 0.1 mmol.) in 1 mL DCM at 0 °C and stirred overnight. Triethylamine (0.6 mL) was added and

reaction mixture was stirred for 1h. Purification was performed via cold column chromatography at 0 °C with 15:1 hexane-DCM. White solid (28 mg) was obtained with yield of 48 %.

$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ +12.2 ($^1J_{\text{PW}} = 244$ Hz). ^1H NMR (CD_2Cl_2): δ 4.23 (m, 2H, CH_2), 6.88 (dd, $^2J_{\text{PH}} = 10.8$ Hz, $^3J_{\text{HH}} = 17.2$ Hz, 1H, PCH=), 7.36 (dd, $^3J_{\text{PH}} = 17.5$ Hz, $^3J_{\text{HH}} = 17.5$ Hz, 1H, $=\text{CHPh}$), 7.41-7.61 (m, 10H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 44.45 (d, $^1J_{\text{CP}} = 19.2$ Hz, CH_2Cl), 120.07 (d, $^1J_{\text{CP}} = 45.0$ Hz, PCH=), 128.04 (s, Ph), 129.38 (s, Ph), 129.40 (d, $J_{\text{CP}} = 9.6$ Hz, Ph), 130.53 (s, Ph), 130.98 (s, Ph), 131.09 (s, Ph), 133.88 (d, $^1J_{\text{CP}} = 44.7$ Hz, ipso Ph), 135.64 (d, $^3J_{\text{CP}} = 16.9$ Hz, ipso Ph), 149.74 (d, $^2J_{\text{CP}} = 13.6$ Hz, $=\text{CHPh}$), 196.72 (d, $^2J_{\text{CP}} = 6.8$ Hz, cis CO), 199.17 (d, $^2J_{\text{CP}} = 22.0$ Hz, trans CO). HRMS: m/z 583.9761 (calcd for $\text{C}_{20}\text{H}_{14}\text{O}_5\text{PClW}$ 583.9777).

Synthesis of **11j**. Procedure similar to literature; 1,3-dichloropropane used instead.^[22]

Yellow solid (25%). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ +3.7 ($^1J_{\text{PW}} = 209$ Hz). ^1H NMR (C_6D_6): δ 1.30 (m, 2H, CH_2), 1.60 (s, 6H, Me), 1.67 (m, 2H, CH_2), 2.89 (t, $^3J_{\text{HH}} = 6.3$ Hz, 2H, CH_2Cl), 5.80 (d, $^2J_{\text{PH}} = 37.0$ Hz, 2H, PCH=). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 16.78 (d, $^3J_{\text{CP}} = 11.1$ Hz, Me), 27.34 (d, $^1J_{\text{CP}} = 24.5$ Hz, PCH_2), 28.61 (d, $^2J_{\text{CP}} = 2.9$ Hz, PCH_2CH_2), 44.63 (d, $^3J_{\text{CP}} = 14.0$ Hz, ClCH_2), 128.39 (d, $^1J_{\text{CP}} = 41.3$ Hz, PCH=), 151.61 (d, $^2J_{\text{CP}} = 8.3$ Hz, $=\text{CMe}$), 196.63 (d, $^2J_{\text{CP}} = 6.8$ Hz, cis CO), 199.36 (d, $^2J_{\text{CP}} = 17.5$ Hz, trans CO). HRMS: m/z 511.9779 (calcd for $\text{C}_{14}\text{H}_{14}\text{O}_5\text{PClW}$ 511.9777).

11j Bright yellow solid (77%). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ +212.4 ($^1J_{\text{PW}} = 236$ Hz). ^1H NMR (C_6D_6): δ 1.93 (m, 2H, CH_2), 1.96 (d, $^4J_{\text{PH}} = 0.9$ Hz, 6H, Me), 2.39 (m, 2H, CH_2), 3.59 (t, $^3J_{\text{HH}} = 6.4$ Hz, 2H, CH_2Cl), 3.61 (d, $^2J_{\text{PH}} = 2.6$ Hz, 2H, PCH), 3.80 (s, 6H, OMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 16.12 (d, $^3J_{\text{CP}} = 1.7$ Hz, Me), 28.31 (d, $^1J_{\text{CP}} = 1.9$ Hz, PCH_2), 33.54 (s, PCH_2CH_2), 45.28 (d, $^3J_{\text{CP}} = 13.6$ Hz, ClCH_2), 52.78 (s, OMe), 59.28 (d, $^1J_{\text{CP}} = 19.9$ Hz, PCH), 139.04 (d, $^2J_{\text{CP}} = 16.0$ Hz, $=\text{CMe}$), 145.54 (d, $^2J_{\text{CP}} = 4.6$ Hz, $=\text{CCO}_2$), 165.41 (d, $^3J_{\text{CP}} = 2.6$ Hz, CO_2), 196.53 (d, $^2J_{\text{CP}} = 6.7$ Hz, cis CO), 198.18 (d, $^2J_{\text{CP}} = 25.4$ Hz, trans CO). HRMS: m/z 654.0034 (calcd for $\text{C}_{20}\text{H}_{20}\text{O}_9\text{PClW}$ 654.0043).

37a White solid (38%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -25.2 ($^1J_{\text{PW}} = 228$ Hz). ^1H NMR (CD_2Cl_2): δ 1.90 (m, 2H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{Cl}$), 2.31 (m, 2H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{Cl}$), 3.55 (t, $^3J_{\text{HH}} = 6.3$ Hz, 2H, CH_2Cl), 5.83 (ddd, $^1J_{\text{PH}} = 339.6$ Hz, $^3J_{\text{HH}} = 6.4$ Hz, $^3J_{\text{HH}} = 6.4$ Hz, 1H, PH), 7.48-7.57 (m, 5H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 27.85 (d, $^1J_{\text{CP}} = 25.9$ Hz, PCH_2), 31.06 (d, $^2J_{\text{CP}} = 4.0$ Hz, PCH_2CH_2), 45.14 (d, $^3J_{\text{CP}} = 13.2$ Hz, ClCH_2), 129.60 (d, $J_{\text{CP}} = 9.8$ Hz, Ph), 131.03 (d, $J_{\text{CP}} = 2.0$ Hz, Ph), 131.79 (d, $^1J_{\text{CP}} = 46.2$ Hz, ipso Ph), 131.97 (d, $J_{\text{CP}} = 7.0$ Hz, Ph), 196.66 (d, $^2J_{\text{CP}} = 7.0$ Hz, cis CO), 199.63 (d, $^2J_{\text{CP}} = 21.2$ Hz, trans CO). HRMS: m/z 509.9624 (calcd for $\text{C}_{14}\text{H}_{12}\text{O}_5\text{PClW}$ 509.9620).

37b White solid (51%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -46.7 ($^1J_{\text{PW}} = 234$ Hz). ^1H NMR (CD_2Cl_2): δ 1.96 (m, 2H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{Cl}$), 2.33 (m, 2H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{Cl}$), 3.58 (t, $^3J_{\text{HH}} = 6.3$ Hz, 2H, CH_2Cl), 6.18 (ddd, $^1J_{\text{PH}} = 345.8$ Hz, $^3J_{\text{HH}} = 6.8$ Hz, $^3J_{\text{HH}} = 4.4$ Hz, 1H, PH), 7.24 (m, 1H, Th), 7.48 (m, 1H, Th), 7.72 (m, 1H, Th). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 29.56 (d, $^1J_{\text{CP}} = 28.2$ Hz, PCH_2), 30.36 (d, $^2J_{\text{CP}} = 1.4$ Hz, PCH_2CH_2), 45.13 (d, $^3J_{\text{CP}} = 14.9$ Hz, ClCH_2), 129.14 (d, $J_{\text{CP}} = 10.3$ Hz, Th), 130.65 (d, $^1J_{\text{CP}} = 41.1$ Hz, ipso Th), 132.93 (d, $J_{\text{CP}} = 2.2$ Hz, Th), 136.50 (d, $J_{\text{CP}} = 10.1$ Hz, Th), 196.43 (d, $^2J_{\text{CP}} = 7.0$ Hz, cis CO), 199.08 (d, $^2J_{\text{CP}} = 22.1$ Hz, trans CO). HRMS: m/z 515.9180 (calcd for $\text{C}_{12}\text{H}_{10}\text{O}_5\text{PClSW}$ 515.9184).

37c White solid (24%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -55.2 ($^1J_{\text{PW}} = 232$ Hz). ^1H NMR (CD_2Cl_2): δ 1.98 (m, 2H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{Cl}$), 2.34 (m, 2H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{Cl}$), 3.59 (t, $^3J_{\text{HH}} = 6.3$ Hz, 2H, CH_2Cl), 6.01 (ddd, $^1J_{\text{PH}} = 349.9$ Hz, $^3J_{\text{HH}} = 5.7$ Hz, $^3J_{\text{HH}} = 5.2$ Hz, 1H, PH), 6.55 (m, 1H, Fu), 6.99 (br s, 1H, Fu), 7.76 (s, 1H, Fu). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 26.45 (d, $^1J_{\text{CP}} = 29.7$ Hz, PCH_2), 30.41 (s, PCH_2CH_2), 45.15 (d, $^3J_{\text{CP}} = 15.2$ Hz, ClCH_2), 111.73 (d, $J_{\text{CP}} = 6.8$ Hz, Fu), 122.37 (d, $J_{\text{CP}} = 17.2$, Fu), 146.06 (d, $^1J_{\text{CP}} = 55.3$ Hz, ipso Fu), 148.73 (d, $J_{\text{CP}} = 4.3$ Hz, Fu), 196.19 (d, $^2J_{\text{CP}} = 7.0$ Hz, cis CO), 198.90 (d, $^2J_{\text{CP}} = 22.2$ Hz, trans CO). HRMS: m/z 499.9415 (calcd for $\text{C}_{12}\text{H}_{10}\text{O}_6\text{PClW}$ 499.9413).

38a White solid (14%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ +29.4 ($^1J_{\text{PW}} = 219$ Hz). ^1H NMR (CD_2Cl_2): δ 2.52-2.81 (m, 6H, CH_2), 7.41-7.59 (m, 5H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 23.87 (d, $^2J_{\text{CP}} = 17.6$ Hz, CH_2), 28.55 (d, $^1J_{\text{CP}} = 35.5$ Hz, PCH_2), 129.05 (d, $J_{\text{CP}} = 10.6$ Hz, Ph), 129.19 (d, $J_{\text{CP}} = 9.2$ Hz, Ph), 129.96 (d, $J_{\text{CP}} = 2.0$ Hz, Ph), 139.95 (d, $^1J_{\text{CP}} = 27.5$ Hz, ipso Ph), 197.19 (d, $^2J_{\text{CP}} = 7.1$ Hz, cis CO), 200.93 (d, $^2J_{\text{CP}} = 21.2$ Hz, trans CO). HRMS: m/z 473.9856 (calcd for $\text{C}_{14}\text{H}_{11}\text{O}_5\text{PW}$ 473.9854).

38b White solid (23%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ +21.7 ($^1J_{\text{PW}} = 221$ Hz). ^1H NMR (CD_2Cl_2): δ 2.56 (m, 4H, PCH_2), 2.74 (m, 2H, CH_2), 7.04 (m, 1H, CH=), 7.19-7.48 (m, 5H, Ph), 7.55 (m, 1H, CH=). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 23.44 (d, $^2J_{\text{CP}} = 17.6$ Hz, CH_2), 28.06 (d, $^1J_{\text{CP}} = 37.0$ Hz, PCH_2), 126.55 (d, $^1J_{\text{CP}} = 45.9$ Hz, PCH=), 127.63 (s, Ph), 129.30 (s, Ph), 129.83 (s, Ph), 135.98 (d, $^3J_{\text{CP}} = 14.5$ Hz, ipso Ph), 142.35 (d, $^2J_{\text{CP}} = 5.2$ Hz, PhCH=), 197.22 (d, $^2J_{\text{CP}} = 7.2$ Hz, cis CO), 200.69 (d, $^2J_{\text{CP}} = 20.9$ Hz, trans CO). HRMS: m/z 499.9999 (calcd for $\text{C}_{16}\text{H}_{13}\text{O}_5\text{PW}$ 500.0010).

Synthesis of phosphetane complex **39**. Sodium hydride (1.2 eq.) was added to 1 mL THF solution of **37b** (or **c**) at 0 °C and the reaction mixture was warmed up to rt over 1 h. Solvent was evaporated and the residue was strained onto silica. Purification was performed via cold column chromatography at 0 °C with 15:1 hexane-dichloromethane.

39a White solid (80%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ +13.3 ($^1J_{\text{PW}} = 229$ Hz). ^1H NMR (CD_2Cl_2): δ 2.74 (m, 6H, CH_2), 7.28 (m, 1H, Th), 7.55 (m, 1H, Th), 7.75 (m, 1H, Th). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 22.67 (d, $^2J_{\text{CP}} = 17.4$ Hz, CH_2), 31.59 (d, $^1J_{\text{CP}} = 37.2$ Hz, PCH_2), 128.95 (d, $J_{\text{CP}} = 9.7$ Hz, Th), 132.34 (d, $J_{\text{CP}} = 1.9$ Hz, Th), 134.54 (d, $J_{\text{CP}} = 10.0$ Hz, Th), 140.02 (d, $^1J_{\text{CP}} = 19.2$ Hz, ipso Th), 197.08 (d, $^2J_{\text{CP}} = 7.1$ Hz, cis CO), 200.20 (d, $^2J_{\text{CP}} = 22.1$ Hz, trans CO). HRMS: m/z 479.9414 (calcd for $\text{C}_{12}\text{H}_9\text{O}_5\text{PSW}$ 479.9418).

39b White solid (79%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ +2.9 ($^1J_{\text{PW}} = 227$ Hz). ^1H NMR (CD_2Cl_2): δ 2.53-2.91 (m, 6H, CH_2), 6.58 (s, 1H, Fu), 7.04 (s, 1H, Fu), 7.81 (s, 1H, Fu). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 22.54 (d, $^2J_{\text{CP}} = 17.8$ Hz, CH_2), 28.57 (d, $^1J_{\text{CP}} = 38.0$ Hz, PCH_2), 111.79 (d, $J_{\text{CP}} = 6.6$ Hz, Fu), 120.91 (d, $J_{\text{CP}} = 17.1$ Hz, Fu), 148.37 (d, $J_{\text{CP}} = 3.4$ Hz, Fu), 152.50 (d, $^1J_{\text{CP}} = 32.4$ Hz, ipso Fu), 196.82 (d, $^2J_{\text{CP}} = 7.3$ Hz, cis CO), 200.01 (d, $^2J_{\text{CP}} = 22.3$ Hz, trans CO). HRMS: m/z 463.9634 (calcd for $\text{C}_{12}\text{H}_9\text{O}_6\text{PW}$ 463.9646).

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Appendix

Table A1. Crystal data and structure refinement for compound **13b**.

Identification code	mat166r	
Chemical formula	C ₁₅ H ₉ O ₅ PSW	
Formula weight	516.1	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.200 x 0.220 x 0.400 mm	
Crystal habit	colorless block	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 8.56880(10) Å	α = 90°
	b = 6.50600(10) Å	β = 90.9458(9)°
	c = 29.2502(5) Å	γ = 90°
Volume	1630.44(4) Å ³	
Z	4	
Density (calculated)	2.103 g/cm ³	
Absorption coefficient	7.331 mm ⁻¹	
F(000)	976	

Theta range for data collection	2.77 to 30.63°
Index ranges	-12<=h<=8, -9<=k<=9, -41<=l<=41
Reflections collected	17482
Independent reflections	5021 [R(int) = 0.0421]
Coverage of independent reflections	99.60%
Absorption correction	multi-scan
Max. and min. transmission	0.3220 and 0.1570
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2013 (Sheldrick, 2013)
Function minimized	$\sum w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	5021 / 276 / 257
Goodness-of-fit on F ²	1.222
$\Delta/\sigma_{\max}$	0.003
Final R indices	4706 data; $l > 2\sigma(l)$ R1 = 0.0332, wR2 = 0.0678
	all data R1 = 0.0370, wR2 = 0.0690
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0103P)^2 + 5.4319P]$ where $P = (F_o^2 + 2F_c^2)/3$
Largest diff. peak and hole	2.159 and -3.847 eÅ ⁻³
R.M.S. deviation from mean	0.238 eÅ ⁻³

Table A2. Crystal data and structure refinement for compound **16**.

Identification code	mat167s	
Chemical formula	$C_{13}H_7O_5PS_2W$	
Formula weight	522.13	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.180 x 0.200 x 0.280 mm	
Crystal habit	colorless block	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	$a = 14.9388(4)$ Å	$\alpha = 90^\circ$
	$b = 6.39280(10)$ Å	$\beta = 90.3114(11)^\circ$
	$c = 16.9565(3)$ Å	$\gamma = 90^\circ$
Volume	$1619.33(6)$ Å ³	
Z	4	
Density (calculated)	2.142 g/cm ³	
Absorption coefficient	7.507 mm ⁻¹	
F(000)	984	
Theta range for data collection	1.82 to 45.38°	

Index ranges	-29<=h<=29, -12<=k<=10, -33<=l<=21
Reflections collected	34255
Independent reflections	13580 [R(int) = 0.0531]
Coverage of independent reflections	99.60%
Absorption correction	multi-scan
Max. and min. transmission	0.3450 and 0.2280
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick 2008)
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2013 (Sheldrick, 2013)
Function minimized	$\sum w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	13580 / 209 / 248
Goodness-of-fit on F ²	0.992
$\Delta/\sigma_{\max}$	0.002
Final R indices	9736 data; $I > 2\sigma(I)$ R1 = 0.0436, wR2 = 0.0866
	all data R1 = 0.0706, wR2 = 0.0981
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0363P)^2 + 0.6432P]$ where $P = (F_o^2 + 2F_c^2)/3$
Largest diff. peak and hole	1.685 and -3.412 eÅ ⁻³
R.M.S. deviation from mean	0.297 eÅ ⁻³

Table A3. Crystal data and structure refinement for compound **32c**.

Identification code	mat195s	
Chemical formula	C ₁₁ H ₇ O ₅ PSW	
Formula weight	466.05 g/mol	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.220 x 0.320 x 0.420 mm	
Crystal habit	colorless block	
Crystal system	orthorhombic	
Space group	P n m a	
Unit cell dimensions	a = 14.3156(11) Å	α = 90°
	b = 8.6472(7) Å	β = 90°
	c = 11.5793(9) Å	γ = 90°
Volume	1433.40(19) Å ³	
Z	4	
Density (calculated)	2.160 g/cm ³	
Absorption coefficient	8.326 mm ⁻¹	
F(000)	872	
Theta range for data collection	3.27 to 33.17°	

Index ranges	-21<=h<=21, -13<=k<=12, -17<=l<=14
Reflections collected	27345
Independent reflections	2879 [R(int) = 0.1393]
Coverage of independent reflections	99.40%
Absorption correction	multi-scan
Max. and min. transmission	0.2620 and 0.1280
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)
Function minimized	$\sum w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	2879 / 0 / 113
Goodness-of-fit on F ²	1.06
$\Delta/\sigma_{\max}$	0.001
Final R indices	2123 data; $I > 2\sigma(I)$ R1 = 0.0636, wR2 = 0.1382
	all data R1 = 0.0950, wR2 = 0.1547
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0568P)^2+17.3101P]$ where $P=(F_o^2+2F_c^2)/3$
Extinction coefficient	0.0055(6)
Largest diff. peak and hole	4.700 and -4.161 eÅ ⁻³
R.M.S. deviation from mean	0.346 eÅ ⁻³

Table A4. Crystal data and structure refinement for compound **39a**.

Identification code	mat196s	
Chemical formula	C ₁₂ H ₉ O ₅ PSW	
Formula weight	480.07 g/mol	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.300 x 0.320 x 0.420 mm	
Crystal habit	colorless block	
Crystal system	orthorhombic	
Space group	P n m a	
Unit cell dimensions	a = 13.7828(6) Å	α = 90°
	b = 9.2209(5) Å	β = 90°
	c = 11.3745(5) Å	γ = 90°
Volume	1445.58(12) Å ³	
Z	4	
Density (calculated)	2.206 g/cm ³	
Absorption coefficient	8.259 mm ⁻¹	
F(000)	904	
Theta range for data collection	3.21 to 42.22°	

Index ranges	-24<=h<=26, -16<=k<=17, -21<=l<=14
Reflections collected	28533
Independent reflections	5318 [R(int) = 0.1618]
Coverage of independent reflections	99.60%
Absorption correction	multi-scan
Max. and min. transmission	0.1910 and 0.1290
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)
Function minimized	$\sum w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	5318 / 241 / 145
Goodness-of-fit on F ²	0.977
Final R indices	3685 data; I>2σ(I) R1 = 0.0561, wR2 = 0.1154 all data R1 = 0.0883, wR2 = 0.1301
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0123P)^2]$ where $P=(F_o^2+2F_c^2)/3$
Extinction coefficient	0.0110(7)
Largest diff. peak and hole	6.117 and -3.687 eÅ ⁻³
R.M.S. deviation from mean	0.486 eÅ ⁻³