New aspects of phosphirane chemistry

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NEW ASPECTS OF PHOSPHIRANE CHEMISTRY

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ABSTRACT

This thesis provides a detailed account of author's exploration on new aspects of phosphirane chemistry. Chapter one briefly reviews the theoretical and experimental works on phosphiranes that have been published until the middle of 2014. Chapter two describes the investigation on the influence of additional strain on phosphiranes. The subjects of the investigation are norbornane-annulated 1-methylphosphirane complexes. The stereochemistry of these complexes has further strained the annulated phosphiranes, leading to a number of structural distortions and selective decomplexation by CO under pressure. Chapter two also recounts the serendipitous discovery of phosphorus dimers from the thermolysis of 7-allyl-7-phosphanorbornadiene complex. Chapter three illustrates the study on the activation of 1-chlorophosphirane by aluminium trichloride. The subject of the study is cyclohexane-annulated 1-chlorophosphirane complex. It undergoes AlCl_3 -catalysed electrophilic aromatic substitution with thiophene and ferrocene to produce 1-(2-thienyl)- and 1-ferrocenylphosphirane complexes respectively. In the absence of electron-rich arenes, a P-C bond cleavage catalysed by AlCl_3 takes place yielding dichloro(cyclohexyl)phosphine complex. The transient ferrocenylphosphinidene complex can be generated from 1-ferrocenylphosphirane complex and trapped with diphenylacetylene, *trans*-stilbene and water.

LIST OF PUBLICATIONS

1. *"Role of Steric Strain in the Chemistry of Phosphiranes"*

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3. *"Activation of a 1-Chlorophosphirane Complex by Aluminium Trichloride. Generation and Trapping of [Fc-P-W(CO)₅] (Fc = Ferrocenyl)"*

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LIST OF ABBREVIATIONS

BABAR-Phos	phosphaazabarbaralene
BSSE	basis set superposition error
COD	1,5-cyclooctadiene
hfacac	hexafluororacetylacetonato
Cp	cyclopentadiene
Cp*	pentamethylcyclopentadiene
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DMAD	dimethyl acetylenedicarboxylate
DFT	density functional theory
ee	enantiomeric excess
ESR	electron spin resonance
Fc	ferrocene
HOMO	highest occupied molecular orbital
i.e.	isto es
IR	infrared
LUMO	lowest unoccupied molecular orbital
<i>n</i> -BuLi	<i>n</i> -butyllithium
NMR	nuclear magnetic resonance

RT room temperature

t-butyl tert-butyl

UV ultraviolet

vs. versus

1.1 Phosphiranes: Introduction

Phosphirane is the simplest of the phosphorus-containing saturated heterocyclic ring systems, bearing one phosphorus and two carbon atoms. While the first preparative method for phosphirane was described in 1963 by Wagner,¹ the discovery was confirmed in 1967 through its characterization by mass, infrared and nuclear magnetic resonance spectra.² Phosphirane compounds have only been known for a relatively short period of time comparing to its oxygen (1859), nitrogen (1888) and sulfur (1916) counterparts (Fig. 1.1).^{3,4}

Figure 1.1 Parent structures of three-membered saturated rings containing one heteroatom

These cyclic compounds have garnered much attention owing to their high strain energy, which promotes a number of unusual ring-opening and ring-expansion reactions. Their distinct reactivity has been employed as entry points to the development of complex heteroatom-containing products in organic synthesis. For example, nucleophilic ring opening of aziridine-2-*t*-butyl carboxylate with primary amines provides *N*-alkylated derivatives of 2,3-diaminopropionic acid, an antibiotic precursor (Scheme 1.1).^{5, 6} The stereoselective copper-catalyzed ring expansion of vinyl oxirane into 2,5-dihydrofuran (Scheme 1.2) has been utilized in the short asymmetric synthesis of natural product (+)-goniothalesdiol from cinnamaldehyde.⁷ Using the same copper(II) catalyst, vinyl thiiranes and vinyl aziridines also perform the rearrangement into their respective five-membered ring products, of which the former product, 2,5-dihydrothiophene, is an intermediate in the total synthesis of biotin.^{8,9}

Scheme 1.1 Ring opening of aziridine-2-*t*-butyl carboxylate by primary amine

Scheme 1.2 Copper-catalyzed ring expansion of vinyl oxirane

These are only a few selected examples of the synthetic utility of saturated three-membered heterocycles. More comprehensive discussions on the advances in this chemistry can be found in multiple review articles.¹⁰⁻¹⁵

In this chapter, author attempts to briefly review the literature on phosphiranes until the middle of 2014. Whereas phosphiranium cation is also mentioned here, the chemistry of phosphiranylium ion will be discussed in another chapter (Fig. 1.2). Three-membered phosphorus heterocycles bearing additional heteroatom(s) in the rings are excluded from this chapter.

Figure 1.2 Structure of phosphiranium and phosphiranylium cations

1.2 Phosphiranes: Structure

Tabulation of most structural data of phosphiranes has been published in several review articles as well.^{4, 16-18} While some parameters were collected from X-ray crystal structure analyses, others were calculated by *ab initio* methods and density functional theory (DFT). Typically, the molecular structures display exceptionally acute intracyclic C-P-C angle, ranging between 46° to 51° . The intracyclic bond distances vary from 178 to 189 pm for P-C and 146 to 159 pm for C-C bonds. Whereas the phosphiranium salt has a similar intracyclic C-P-C angle (51.7°) and C-C bond length (153 pm), its P-C bonds are slightly shortened (176 pm).¹⁹

Likewise any three-membered ring systems, phosphiranes are explicitly characterised by their extreme high-field ^1H , ^{13}C and ^{31}P NMR shifts as well as the large $^1J_{\text{CP}}$ coupling constants.

The upfield shift of the ^{31}P resonance has been correlated with the huge HOMO/LUMO energy gap and the decreased p-character of the phosphorus lone pair.²⁰ Besides the characteristic NMR features, other spectroscopic studies including infrared and combined IR-Raman studies have been described.²¹⁻²⁴

Phosphiranes have been the topic of numerous theoretical investigations. The calculations indicate that phosphorus and carbon atoms bear significant positive and negative partial charges respectively.^{25, 26} The same studies have also demonstrated that the HOMO corresponds to the phosphorus lone pair, while the HOMO-1 and LUMO, resulting from the bonding and antibonding combinations of $p_{(\text{P})}$ and $\pi^*_{(\text{C}=\text{C})}$, are associated with the $\sigma(\text{P}-\text{C})$ bent bonds (Fig. 1.3).

Figure 1.3 Molecular orbitals for parent phosphirane²⁶

The inherent ring strain energy of phosphirane has been calculated at the MP2/6-31G(d) level to be larger than that of thiirane ($-22.0 \text{ kcal mol}^{-1}$ vs. $-17.7 \text{ kcal mol}^{-1}$), but lower than that of oxirane ($-30 \text{ kcal mol}^{-1}$) and aziridine ($-29.5 \text{ kcal mol}^{-1}$).²⁷ Another study has predicted that there is a substantial increase in the strain energy of phosphirane upon protonation.²⁸ Meanwhile, the computed fragmentation enthalpy of phosphirane into heteroatomic subunit (PH) and ethylene is rather low ($72.3 \text{ kcal mol}^{-1}$), compared to thiirane ($84.3 \text{ kcal mol}^{-1}$), aziridine ($109.7 \text{ kcal mol}^{-1}$) and oxirane ($128.7 \text{ kcal mol}^{-1}$) at the MP2/6-31G(d) level.²⁷ Additionally, one calculation has shown that the rearrangement of phosphirane into vinylphosphine has only a small energy barrier of $56.2 \text{ kcal mol}^{-1}$ at the QCISD(T)/6-31G(d,p)+ZPE level.²⁹ These findings depict phosphiranes as species that are thermodynamically moderately stable but still prone to rearrangements and ring-fragmentation reactions. Since then, several other theoretical studies

have been carried out at different levels of theory and they are in remarkable agreement with the thermodynamical parameters presented above.²⁹⁻³³

1.3 Phosphiranes: Reactivity

1.3.1 Reactions with Cleavage of One Intracyclic P-C Bond

As stated earlier, the theoretical studies revealed that the P-C bonds of the phosphirane ring are high in energy and polarized in a way that there is a partial positive charge at phosphorus and a partial negative charge at carbon. In consequence, phosphiranes undergo intriguing ring cleavage reactions, which can be grouped into four, based on the reaction mechanisms.

1.3.1.1 Electrophilic Attack at Ring Carbon

When phosphiranes are treated with protic reagents, ring cleavage can take place via electrophilic attack at the carbon of the ring. For instance, bicyclic phosphirane, whose P-C bond polarization is enhanced by the nitrogen substituent at phosphorus, was easily cleaved at room temperature by hydrogen chloride or methanol (Scheme 1.3).³⁴

Scheme 1.3 Ring cleavage by HCl or MeOH at room temperature

However, the polarity is reversed when there is a substituent bearing a lone pair on the ring carbon. As a result, the proton is found at phosphorus after hydrolysis (Scheme 1.4).^{35, 36}

Scheme 1.4 Hydrolysis of phosphirane with lone-pair-bearing substituent on ring carbon

Besides, upon treatment with dichlorophosphines, the ring opening of phospha[3]-radialenes took place, involving electrophilic attack at the carbon of the ring (Scheme 1.5).³⁷

Scheme 1.5 Reaction of phospha[3]radialenes with dichlorophosphines

1.3.1.2 Proton Abstraction at Ring Carbon

When the attacking nucleophiles are highly basic and sterically bulky, the ring-opening of phosphiranes tend to proceed via deprotonation of one carbon of the ring. Examples of this mechanism have been reported by Quast (Scheme 1.6)³⁸ and Mathey (Scheme 1.7)³⁹.

Scheme 1.6 Ring-opening of phosphirane oxide by lithium amide

Scheme 1.7 Ring opening of phosphirane tungsten complex by lithium amide

Recently, a 1-phospha-pentadienyl complex has been synthesised from a 2-vinylphosphirane complex by utilizing this selective metalation (Scheme 1.8).⁴⁰

Scheme 1.8 Synthesis of 1-phospha-pentadienyl complex from 2-vinylphosphirane complex

1.3.1.3 Nucleophilic Attack at Phosphorus

Ring-opening of phosphiranes also takes place via nucleophilic attack at phosphorus when a weaker and less hindered base is used, such as PhNHLi, Ph₂NLi, and NaOEt. (Scheme 1.9).³⁹

Scheme 1.9 Ring-opening of phosphirane complex via nucleophilic attack at phosphorus

The ring-opening mechanism involves formation of a transient phosphorane which is then followed by reorganisation of the transient species (Scheme 1.10).⁴

Scheme 1.10 Mechanism of ring opening of phosphiranes

Another example of this mechanism has been illustrated by Richter with vinylphosphirane (Scheme 1.11).⁴¹

Scheme 1.11 Reaction of vinylphosphirane with methylenetriphenylphosphorane

1.3.1.4 Ring-Chain Rearrangement

In 1992, Mathey et al observed the existence of an equilibrium between 1-vinylphosphirane and divinylphosphine above 500°C during their study of flash thermolysis of 1-vinylphosphirane (Scheme 1.12).⁴² Afterwards, Nguyen and co-workers performed theoretical study on the equilibrium and found the phosphirane-vinylphosphine rearrangement to be a concerted process.²⁹ The P-C bond cleavage and the 1,3-hydrogen shift from C to P take place concurrently in a single transition structure.

Scheme 1.12 Phosphirane-vinylphosphine rearrangement

However, in the case of 2-halophosphirane complex, the ring opening occurs simultaneously with [1,3] halogen shift instead of hydrogen migration (Scheme 1.13).^{43, 44} These experimental findings are contrasting with the theoretical calculations presented by Nguyen and co-workers, which favor migration of hydrogen over that of halogen.⁴⁵ The calculations were carried out on uncomplexed phosphiranes, hence, the presence of $W(CO)_5$ may induce a different reaction mechanism.

Scheme 1.13 Rearrangement of 2-chlorophosphirane into vinylchlorophosphine

Meanwhile, concerted ring cleavage with migration of a halo substituent was also found in the synthesis of triafulvene, with phosphaspiropentene as the transient intermediate (Scheme 1.14).⁴⁶

Scheme 1.14 Synthesis of triafulvene with phosphaspiropentene as intermediate

Ring cleavage has also been observed in phosphiranium chemistry. Phosphiranium salt reacts with water and primary alcohol to give ring-opening products (Scheme 1.15).¹⁹ Meanwhile, cationic ring-opening polymerisation can also take place when the nucleophile is the phosphirane itself (Scheme 1.16).⁴⁷

Scheme 1.15 Ring opening of phosphiranium salt

Scheme 1.16 Cationic ring-opening polymerisation of phosphirane

1.3.2 Reactions with Cleavage of Two Intracyclic P-C Bonds

The first fragmentation of phosphirane by the simultaneous thermal cleavage of two intracyclic P-C bonds was studied by Quast (Scheme 1.17).⁴⁸ He suggested that the cleavage reaction was concerted when the retention of stereochemistry of the olefinic fragment was observed.

Scheme 1.17 Thermal cleavage of phosphirane oxide

Another convincing example of the thermal splitting of phosphirane was presented by Niecke, with chloro(methylene)phosphine being characterised as the product (Scheme 1.18).⁴⁹

Scheme 1.18 Thermal splitting of phosphirane yielding chloro(methylene)phosphine

Gaspar and co-workers have also studied the cycloreversion of 1-mesitylphosphirane by means of thermal (190°C) and photochemical decomposition.⁵⁰ The 254-nm photolysis of 1-mesitylphosphirane yielded oligomers of mesitylphosphinidene (cyclo-(MesP)₃ and cyclo-(MesP)₄) as major products. However, in the presence of alkene and alkyne, the yield of phosphinidene oligomers was reduced and formation of three-membered rings was observed (Scheme 1.19). Later, the mesitylphosphinidene from the photolysis was successfully observed by ESR spectroscopy.⁵¹ Additional data on the photolysis of bulky 1-arylphosphirane producing phosphinidene can be found in the work of Yoshifuji.⁵²

Scheme 1.19 Photolysis of 1-mesitylphosphirane in the presence of alkene and alkyne

A computational study by Nguyen demonstrated that the cycloreversion of phosphirane to give an alkene and a phosphinidene is a feasible mode of fragmentation ($\Delta H = 74 \text{ kcal mol}^{-1}$).²⁹ The thermal splitting of several phosphirane tungsten complexes and phosphiranium salt was also found to be in accordance with previous experimental findings.⁵³⁻⁵⁶

In some cases, the fragmentation of phosphiranes also was observed upon reaction with nucleophiles. For instance, the reaction of organolithium reagents with heavily substituted phosphiranes led to the splitting of the three-membered rings (Scheme 1.20).^{49, 57} Treatment of

phosphirane tungsten complexes with soft nucleophiles leads to ring collapse as well (Scheme 1.21).³⁹

Scheme 1.20 Example of phosphirane splitting by organolithium reagents

Scheme 1.21 Reaction of phosphirane tungsten complexes with soft nucleophiles

Similar to the ring-opening of phosphirane by hard nucleophiles, this splitting reaction by soft nucleophiles also involves the formation of transient pentacoordinate phosphirane. But, the transient phosphorane is not stable enough for the reorganisation to take place. Consequently, simultaneous cleavage of two P-C bonds occurs, leading to the splitting of phosphirane (Scheme 1.22).⁴

Scheme 1.22 Mechanism of the splitting of phosphirane

1.3.3 Ring-Expansion Reactions

Ring expansion of phosphiranes can be performed through intramolecular reorganisation or insertion reactions. The first ring expansion by intramolecular reorganisation was discovered by Richter, where 2-vinylphosphiranes rearranged into phospholenes (Scheme 1.23).^{58, 59} 2-vinyl-phosphiranes can isomerise photochemically by UV irradiation (280 nm), thermally at 150°C or catalytically with Ni⁰ or Pd⁰ complexes.

Scheme 1.23 Intramolecular ring expansion of 2-vinylphosphirane

Richter has also conducted a kinetic study on the thermal isomerisation of 1-*t*-butyl-2-vinylphosphirane and suggested a two-step biradical mechanism (Scheme 1.24).⁶⁰ Later, however, based on density functional theory study, Lammertsma has postulated that the vinylphosphirane-phospholene rearrangement is a concerted reaction while the *cis-trans*-isomerisation is biradical process.⁶¹

Scheme 1.24 Proposed mechanism for intramolecular ring expansion based on kinetic study

A similar thermal reorganisation has also been described for 2-vinylphosphirane tungsten complex (Scheme 1.25).³⁵ More interestingly, 1,2-divinylphosphirane tungsten complex would ring-expand into a 7-membered ring via a concerted phospho-Cope rearrangement (Scheme 1.26).⁶² The reactive phosphalkene was isolated as a [4+2] cycloadduct after reaction with conjugated diene.

Scheme 1.25 Reorganisation of 2-vinylphosphirane tungsten complex

Scheme 1.26 Phospha-Cope rearrangement of 1,2-divinylphosphirane tungsten complex

In addition, the intramolecular ring expansion has also been found to occur for bicyclic phosphiranes. Katz was the first to study the [1,5]-sigmatropic shift of 9-phospha-bicyclo[6.1.0]nonatrienes, which was further investigated by Richter and Quin (Scheme 1.27).⁶³⁻⁶⁵

R = Ph, supermesityl, cyclohexyl, menthyl, *t*-Bu

Scheme 1.27 Ring expansion of 9-phospha-bicyclo[6.1.0]nonatrienes

Thereafter, Quin and Richter also discovered that some of the 9-phospha-bicyclo[6.1.0]nonatriene derivatives would undergo a different rearrangement, involving electrocyclic ring-opening and intramolecular [4+2]-cyclisation to give *trans*-dihydrophosphindoles (Scheme 1.28).^{64, 65} Recently, Lammertsma has reported that 9-phenyl-9-phospha-bicyclo[6.1.0]nonatriene is a remarkably dynamic molecule that undergoes [1,7]-sigmatropic shift in solution at room temperature.⁶⁶

On the other hand, upon quaternisation, the corresponding salt would restructure into 9-phosphabarbaralanes.⁶⁷ Markl has proposed that the restructuring, in fact, also occurred via formation of a phosphonin intermediate (Scheme 1.29).

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Scheme 1.28 Electrocyclic ring-opening and [4+2] ring-closure of 9-phosphabicyclo[6.1.0]nonatrienes

Scheme 1.29 Rearrangement of 9-phosphabicyclo[6.1.0]nonatriene into 9-phosphabarbaralane

Another example of intramolecular ring expansion can be seen from the equilibrium between the bicyclic 1-phosphanorcaradiene and 2*H*-phosphepine. The equilibrium is so shifted toward the bicyclic compound that 2*H*-phosphepine cannot be detected spectroscopically; only 1-chlorodihydrophosphepine can be isolated upon reaction with hydrogen chloride (Scheme 1.30).⁶⁸

Scheme 1.30 Intramolecular ring expansion of 1-phosphanorcaradiene

Lammertsma and co-workers have observed the rearrangement of a bicyclic vinylphosphirane complex into phospholene complex with complete inversion at phosphorus (Scheme 1.31).^{61, 69, 70} Upon heating, the *syn*-vinylphosphirane complex would reorganise into *syn*-phospholene complex in a concerted pericyclic manner whereas the *anti*-vinylphosphirane complex would epimerize into its *syn*-isomer via biradical ring opening-ring closure process.

Scheme 1.31 Rearrangement of bicyclic vinylphosphirane complex

A more recent finding included the reorganisation of *exo*-2-phosphabicyclo[1.1.0]butane into 3-phosphacyclobutene and phospholene via the formation of the 1-phosphabutadiene intermediate (Scheme 1.32).⁷¹

Scheme 1.32 Reorganisation of *exo*-2-phosphabicyclo[1.1.0]butane

In the meantime, the study on ring expansion of phosphiranes by insertion reactions has not been extensive, compared to that of intramolecular rearrangements. The first example was illustrated by Mathey and co-workers when they inserted a vinyl ether into an activated P-C bond of a phosphirane yielding a five-membered ring phospholane.³⁵ [3+2]-cycloadduct was also formed when they reacted 2-alkylidenephosphirane with norbornene or dimethyl acetylenedicarboxylate (DMAD) in the presence of a Pd catalyst (Scheme 1.33).⁷²

Scheme 1.33 Reaction of 2-alkydenephosphirane with norbornene and DMAD

It has been demonstrated that some 14-electron metal fragments also insert into phosphiranes to give phosphametallocyclobutanes (Scheme 1.34).^{73, 74} The insertion reaction proceeds via η^2 -coordination of a P-C bond to the metal centre with the configuration of the starting phosphirane being preserved.

Scheme 1.34 Insertion of 14-electron metal fragments into phosphiranes

1.3.4 Reactions at Phosphorus with Retention of the Cyclic Structure

Despite their tendency to perform ring cleavage reactions for strain relief, phosphiranes do react like other acyclic phosphines. Oxidation, sulfurization and quaternisation of phosphiranes as well as their coordination to transition metals have been reported. In the 1980s, Quin and coworkers studied the oxidation of bicyclic phosphiranes and demonstrated that steric effect plays a role in stabilising the phosphirane oxide.^{65, 75, 76} When they attempted to oxidise 9-phenyl- or 9-*t*-butylphosphabicyclo[6.1.0]nonatriene, the ring collapsed. Using 2,4,6-tri-*t*-butylphenyl as the substituent on phosphorus, they then managed to isolate the oxidation product (Scheme 1.35).⁶⁵

Scheme 1.35 Oxidation of 1-supermesitylphosphirane

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Gaspar and co-workers have converted 2,6-dimethoxyphenylphosphirane to its oxide and sulfide simply by treating it with 30% hydrogen peroxide and sulfur respectively.⁷⁷ Early on, Arbuzov has also reported the formation of phosphirane sulfide by sulfurization (Scheme 1.36).⁷⁸

Scheme 1.36 Sulfurization of phosphirane

The work of Maercker and Brieden showed that quaternisation of phosphirane can take place even though the nucleophilicity of its phosphorus lone pair is very weak (Scheme 1.37).³⁷ However, placing a phenyl substituent on phosphorus gave a ring-opening product.

Scheme 1.37 First quaternisation of phosphirane

Later, 1-methyl-1-phenylphosphiranium salt was successfully prepared and characterised by Wild and co-workers (Scheme 1.38).¹⁹

Scheme 1.38 Reaction of 1-phenylphosphirane with methyl triflate

Meanwhile, the unstable pentacoordinated derivative of phosphirane was detected when 1-phenylphosphirane was treated with dioxetane at -80°C (Scheme 1.39), but it decomposed upon warming up to room temperature.⁷⁹

Scheme 1.39 Treatment of 1-phenylphosphirane with dioxetane

η^1 -coordination of phosphirane to transition metal has also been studied since, in most cases, complexation of the phosphorus lone pair could produce additional ring stability. Plenty examples of such stable complexes, prepared from preformed phosphiranes, have been described (Fig. 1.4).⁸⁰⁻⁸⁶

Figure 1.4 Examples of phosphirane complexes obtained from preformed phosphiranes

It is important to take note that the "tweezer-like" *cis*-PtCl₂ complex displays novel intramolecular π -stacking interactions between the anthracene moieties in the solid state.⁸⁵ This stacking functionality is known to be involved in DNA intercalation for various drugs and antibiotics.⁸⁷ Therefore, it is highly possible that this compound, with mild modifications, can demonstrate active cytotoxicity, like the *cis*-platinum(II) complexes found by Rosenberg.⁸⁸ Generally, strained phosphiranes are not used as phosphine ligands in catalysis because of their lability. The first investigation of their potential role in catalysis was conducted by Mathey et al. Rhodium(I) complex of chiral 1-*l*-menthyl-2-phenylphosphirane has been synthesised and employed in the catalytic hydrogenation of olefins. In spite of ligand decomposition at the end of the reaction, an effective catalytic activity was observed with significant optical yield.⁸²

To improve the stability of phosphiranes, the Grützmacher group incorporated a PC₂ ring into a polycyclic framework, resulting in a more robust phosphirane named BABAR-Phos (Fig. 1.5).⁸⁹ Rhodium(I) and platinum(0) complexes of BABAR-Phos have been synthesised and proven to be active hydrosilylation and hydroboration catalysts respectively.^{90, 91}

Figure 1.5 Structure of BABAR-Phos

More recent examples of using phosphiranes in transition metal catalysed reactions can be found in the work of Maas and co-workers.⁹² Phosphirano-diazaphospholes, previously prepared by Arbuzov et al,⁷⁸ has been introduced as ligands in palladium-catalysed Suzuki cross-coupling of 4-bromotoluene with benzenboronic acid. These compounds mark the first isolated palladium complexes of phosphiranes (Fig. 1.6). A year later, Higham reported the synthesis of remarkably air-stable chiral phosphiranes (Fig. 1.7) and the preliminary investigation of their palladium complexes showed promising catalytic activity in hydrosilylation reaction.⁹³

Figure 1.6 The first Pd complex of phosphiranes

Figure 1.7 Air-stable chiral phosphirane

In addition to transition metals, P-complexation has been extended to boron. Despite being a weak σ -donor, phosphirane has been surprisingly successfully coordinated to borane. Formation of phosphirane-borane complex was first detected by the Kubiak group through ³¹P NMR monitoring (Scheme 1.40).⁸⁴ However, attempts to isolate the borane adducts were unsuccessful. Later, Guillemin and Veszpremi suggested that phosphirane-BH₃ complexes are kinetically very unstable compounds. Once they reacted the parent phosphirane with diborane

at -60°C , the corresponding borane complex was selectively condensed in vacuo and stored at -78°C .

Scheme 1.40 Formation of first phosphirane- BH_3 complex

As 1-chlorophosphiranes have become more accessible,^{49, 57, 94-97} numerous nucleophilic substitution reactions with ring retention have been studied. Metalation of 1-chlorophosphirane is a powerful synthesis tool for a huge variety of phosphirane derivatives (Scheme 1.41).^{49, 97, 98}

Scheme 1.41 Metalation of 1-chlorophosphiranes

Meanwhile, treatment of 1-chloro-2,2,3-tris(trimethylsilyl)phosphirane with base such as, methylenetriphenylphosphorane and DBU, also led to substitution of the chlorine atom, instead of formation of 2*H*-phosphirene (Scheme 1.42).

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Scheme 1.42 Reaction of 1-chlorophosphirane with methylenetriphenylphosphorane and DBU

On the other hand, the metalation of P-H bond of parent phosphirane could only be achieved with the stabilising effect of the transition metal coordination sphere (Scheme 1.43).⁸⁰

Scheme 1.43 Metalation of complexed parent phosphirane

1.4 Phosphiranes: Synthesis

1.4.1 Formation of One P-C Bond and One C-C Bond

Phosphiranes can be prepared by consecutive formation of one P-C bond and one C-C bond from the addition of carbenes to phosphalkenes $RP=CR'_2$. When diazoalkane is used as the carbene source, [3+2] cycloaddition of diazoalkane with phosphalkene gives diazaphosphole, of which the N_2 elimination affords phosphirane.^{57, 92, 96, 99-108} This cycloaddition can be exemplified with the reaction between 1-alkyl-1,2-diphosphole and diphenyldiazomethane (Scheme 1.44).¹⁰⁸

Scheme 1.44 Reaction of 1-alkyl-1,2-diphosphole and diphenyldiazomethane

Besides diazoalkanes, dichlorocarbene¹⁰⁹⁻¹¹³ and organometallic carbenoids⁴⁹ have also been utilized to produce phosphiranes (Scheme 1.45). A similar approach has been developed by Weber when he substituted carbene with isocyanide (Scheme 1.46).¹¹⁴

Scheme 1.45 Reaction between dichlorocarbene and phosphalkene **Scheme 1.46** Isocyanide addition to metallophosphalkene

1.4.2 Formation of One C-C bond

Synthesis of phosphirane by the route of a C-C bond formation takes place during the cyclisation of bisylides (Scheme 1.47).¹¹⁵⁻¹¹⁸

Scheme 1.47 Cyclisation of bisylides

Additionally, in the presence of base, α -haloalkylphosphine oxide rearranges into phosphirane oxide by forming a C-C bond (Scheme 1.48).^{38, 119, 120}

Scheme 1.48 Base-induced rearrangement of α -haloalkylphosphine oxide

An interesting phenomenon was observed while performing the reaction of dialkynylphosphine with zirconocene (Scheme 1.49).¹²¹ The resulting compound is different from the other oxidative alkyne coupling products described in literature.¹²²⁻¹²⁴

Scheme 1.49 Reaction of dialkynylphosphine with zirconocene to give
zirconacyclopentadienophosphirane

In 2005, Lammertsma and coworkers discovered that upon heating, the 3*H*-benzophosphepine complex would undergo a facile electrocyclic reaction to phosphanorcaradiene. However, the latter is unstable and subsequently dissociates into transient phosphinidene complex and naphthalene (Scheme 1.50).¹²⁵

Scheme 1.50 Electrocyclic reaction of 3*H*-benzophosphepine complex to phosphanorcaradiene

1.4.3 Formation of One P-C Bond

One of the synthetic methods for phosphirane includes construction of one P-C bond. Generally, the reaction mechanism involves the cyclisation of deprotonated β -haloalkylphosphines (Scheme 1.51).^{97, 126-129} Other than halogens, there are also examples of tertiary amines as leaving groups.¹³⁰

Scheme 1.51 Cyclisation of deprotonated β -haloalkylphosphine

Meanwhile, a few different approaches have also been described in the literature. Satge and co-workers have observed the contraction of a five-membered ring into phosphirane¹³¹ (Scheme 1.52) and the Mathey group has recounted the self-alkylation of a phosphaylid yielding a phosphirane⁹⁵ (Scheme 1.53).

Scheme 1.52 Contraction of a five-membered ring into phosphirane

Scheme 1.53 Self-alkylation of a phosphaylid to give phosphirane

An exotic example can be seen from the reductive elimination of a nickel metallacycle to give the corresponding phosphirane (Scheme 1.54). The nickelacycle has been synthesised via [2+2] cycloaddition of a nickel phosphinidene complex to ethylene.¹³²

dmp = 2,6-dimesitylphenyl

Scheme 1.54 Reaction of nickel phosphinidene complex with ethylene

Very recently, there has been an account of cyclisation of nucleophilic phosphide intermediates (Scheme 1.55).¹³³ It is proposed that the phosphate would coordinate both the boronic acid and phosphinidene complex, allowing the transfer of the aryl group.

Scheme 1.55 Cyclisation of nucleophilic phosphido intermediates

1.4.4 Formation of Two P-C Bonds

In the meantime, a more popular method for generating phosphirane is through formation of two P-C bonds. The first synthetic approach is by reaction of metallic derivatives of phosphines with 1,2-dichloroalkanes.^{21, 54, 83-85, 134-136} The pioneering work on phosphirane by Wagner is exemplary (Scheme 1.56).^{1, 2}

Scheme 1.56 Reaction of 1,2-dichloroethane with sodium dihydrophosphide

The latest addition to this synthetic route can be found from the work of Higham and co-workers (Scheme 1.57).⁹³ It has been demonstrated that 1,2-dihalides can be replaced by 1,2-dimesylate,¹³⁷ ditosylate^{50, 52, 138, 139} and oxiranes^{55, 82, 140, 141}.

Scheme 1.57 Synthesis of chiral phosphiranes carrying a binaphthyl backbone

In a similar fashion, 1,2-dichloroalkanes have been reacted with zirconocene-phosphinidene complex (Scheme 1.58).¹⁴⁰

Scheme 1.58 Reaction of 1,2-dihaloalkane with zirconocene-phosphinidene complex

The second synthetic route involves the alkylation of dihalophosphines by 1,2-dimetallated alkanes.^{37, 58, 59, 63, 64, 142-144} An example of this method can be well illustrated by the reaction of dipotassium cyclooctatetraenide with dichlorophosphines (Scheme 1.59).⁶³ A more recent study includes the preparation of phosphirane from dichlorophenylphosphine and phosphoryl-stabilised zirconacyclopentane.¹⁴⁵

Scheme 1.59 Reaction of dipotassium cyclooctatetraenide with dichlorophosphines

Finally, the third synthetic pathway for phosphirane is through condensation of transient terminal phosphinidenes with olefins (Scheme 1.60). Very recently, the transient phosphinidene

complex was successfully detected by a series of gas-phase mass spectrometric experiments and was shown to give [1+2] cycloadducts with olefins.¹⁴⁶ Generally, the [1+2] cycloaddition reactions are performed with full retention of the olefinic stereochemistry. Whereas the efficient precursor of free terminal phosphinidene remains limited,^{50, 51, 147-149} the more readily available terminal phosphinidene complexes have given rise to a convenient route to coordinated phosphiranes. Extensive work on generation of terminal phosphinidene complexes has been discussed in several book sections and review articles.¹⁵⁰⁻¹⁵⁷ Several decomplexation techniques have also been developed to obtain the free phosphiranes from the coordinated ones.¹⁵⁸⁻¹⁶⁰

Scheme 1.60 Condensation of transient terminal phosphinidenes with olefins

The transient phosphinidenes have been successfully transposed to various olefins, for instance, styrene and stilbene,^{35, 161, 162} cycloalkenes,^{35, 50, 71, 149, 161} methylenecycloalkanes,^{163, 164} conjugated dienes,^{50, 69, 149, 165-167} allenes,¹⁵⁸ cyclic dienes,^{70, 168, 169} bicyclopropylidene,³¹ norbornadiene,¹⁷⁰ trienes,¹⁷¹ as well as enamines,³⁶ enol ethers and acrylic esters.³⁵ Additionally, oxiranes and ethoxyacetylene have also been reacted with phosphinidene complexes to give the corresponding coordinated phosphiranes.^{172, 173} A *P,C*-cage compound containing phosphirane moiety has been produced following a phosphinidene group transfer to alkyne and its subsequent intramolecular addition (Scheme 1.61).¹⁷⁴

Scheme 1.61 Reaction of phosphinidene complex with alkyne and its subsequent cycloaddition

Furthermore, detailed accounts of self-condensation of transient phosphinidenes bearing olefinic substituent yielding phosphiranes have been reported.^{89, 175-178} Two most recent examples of the intramolecular cycloaddition of phosphinidenes can be depicted by the

synthesis of bidentate phosphorus baskets (Scheme 1.62) and tricyclic phosphiranes (Scheme 1.63).^{177, 178}

Scheme 1.62 Synthesis of bidentate phosphorus baskets

Scheme 1.63 Synthesis of tricyclic phosphirane

Lastly, one phosphiranium salt has been prepared from intramolecular [1+2] cycloaddition of phosphonium ion, R_2P^+ , to alkene (Scheme 1.64).⁹⁰

Scheme 1.64 Intramolecular addition of phosphonium ion to alkene

1.5 Conclusion

The highly strained saturated three-membered phosphacycles are intriguing compounds. While some phosphiranes may decompose at room temperature, others are extremely stable and have been exploited as ligands in homogenous catalysis. Their unique reaction behaviour has enabled an easy access to the discovery of novel compounds and new synthetic routes. Thereupon, it is not far-fetched to conclude that the chemistry of phosphiranes has evolved into an indispensable tool in organophosphorus chemistry. In the next chapters, author aims to study the influence of additional strain on phosphiranes as well as the activation of 1-chloro-phosphiranes by Lewis acids.

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2.1 Introduction

In the ensuing years, significant progress has been made toward understanding the electronic properties and reactivity of phosphirane. As described in the previous chapter, the inherent strain of phosphirane is mainly responsible for its unique chemistry. Therefore, it is of paramount interest to investigate the influence of additional strain on phosphiranes, which is the main subject of this chapter.

One possible way to introduce extra strain on phosphirane is by incorporating P into two units of three-membered ring to form 1-phosphabicyclo[1.1.0]butane (Fig. 2.1). The strain energy contained within this structure is expected to be more than twice the strain energy of a parent phosphirane. For comparison, the strain energy of its carbon analog has been calculated to be $63.9 \text{ kcal mol}^{-1}$ while that of cyclopropane is $27.5 \text{ kcal mol}^{-1}$.¹

Figure 2.1 Structure of 1-phosphabicyclo[1.1.0]butane

To date, much less is known about the existence of phosphorus-substituted bicyclobutanes which do not contain P-P bond. Whereas a few derivatives of 2-phospha- and 2,4-diphosphabicyclo[1.1.0]butanes have been synthesized,²⁻⁷ there is only one derivative of bicyclobutane containing phosphorus at bridgehead position, namely azaphosphabenzvalene. Regitz et al has described that azaphosphabenzvalene can be generated from irradiation of 1,4-azaphosphabenzene (Scheme 2.1).⁸ Nevertheless, a number of theoretical studies on phosphabenzvalene have been published,⁹⁻¹² including one wherein computation showed that the electrocyclic ring opening of *trans*-Dewar phosphabenzene could potentially lead to phosphabenzvalene (Scheme 2.2).¹² The former part of this chapter thus aims to recount

author's attempt to develop highly strained 1-phospha-bicyclo[1.1.0]butane and the serendipitous discovery along the way.

Scheme 2.1 Generation of azaphosphabenzvalene

Scheme 2.2 Ring-opening of *trans*-Dewar phosphabenzene

In addition to increasing the angle strain, introducing steric strain on phosphirane can potentially influence the chemistry of phosphirane as well. As mentioned in the previous chapter, Quin has demonstrated that the steric effect of the supermesityl substituent on phosphorus would stabilise phosphirane oxide against ring-opening.¹³ In another case, BABAR-Phos, of which the phosphirane ring is embedded in a polycyclic cage, is resistant to strong quaternising agents like methyl triflate, unlike monocyclic phosphirane.¹⁴ These examples showcase the steric effect, thus provoking an investigation of the potential role of steric strain in a polycyclic system.

Earlier, condensation of complexed phosphinidene with bicycloalkenes, such as norbornadiene and norbornene, has been illustrated by Lammertsma and co-workers.¹⁵ With the cycloaddition exclusively taking place on the *exo* side of the norbornene, the stereochemistry of the [1+2] cycloadduct allows the investigation of the influence of steric strain exerted by norbornane bridge on the annulated phosphirane. This corresponding investigative study is reflected later in this chapter as well.

2.2 Results and Discussion

Several reports on the self-condensation of phosphinidenes containing olefinic substituent have been outlined in the previous chapter. One particular work has given an account of the self-condensation of 4-pentenylphosphinidene complex **2** into a bicyclic complex with the phosphorus atom at the fused-ring junction **3** (Scheme 2.3).¹⁶ Decomposition of 7-(4-pentenyl)-7-phosphanorbornadiene complex **1** proceeded cleanly to give compound **3**, even in the presence of trapping reagents such as alkynes. Generally, phosphinidene complexes react with alkenes and alkynes to produce phosphiranes and phosphirenes.¹⁷⁻¹⁹

Scheme 2.3 Self-condensation of 4-pentenylphosphinidene complex **2**

However, instead of bicyclobutane, the same study has tentatively proposed a tricyclic complex **6** as the product from self-condensation of allylphosphinidene complex **5**, as deduced from the recorded NMR and mass spectra (Scheme 2.4).¹⁶

Scheme 2.4 Reported self-condensation of allylphosphinidene complex **5**

Aiming at preparing 1-phosphabicyclo[1.1.0]butane thus prompted a re-investigation of this self-condensation of allylphosphinidene complex **5**, starting with a DFT theoretical study on the system. Unexpectedly, no local minimum corresponding to complex **5** could be found using B3PW91/6-31G(d)-Lanl2dz (W).²⁰ the phosphinidene could be found. Instead, the computation led to complex **7** (Fig. 2.2).

Figure 2.2 Computed structure of complex **7**. Selected distances (Å) and angles (deg.): P1-W15 2.549, P1-C12 1.919, P1-C16 1.934, P1-C18 1.919, C12-C16 1.456, C12-C18 2.378; C12-P1-C16 44.4, P-C12-C16 68.4, C12-C16-C18 109.5, W15-P1-C12 123.4, W15-P1-C16 110.1.

Complex **7** would be the product of the intramolecular cycloaddition between phosphinidene phosphorus and the allyl double bond. The computed CPC intracyclic angle of 44.4° is more acute than that of typical phosphiranes (46° - 51°), indicating the high angle strain of the system. Other interesting features of this structure are the high positive charge borne by P: +0.40 (Mulliken charge) and the HOMO which mixes the lone pair at P and a p orbital at the central carbon. It is to be highlighted that such structures have not been described in the literature.

Nevertheless, it remains to be explained why the trapping reactions¹⁶ of allylphosphinidene complex **5** with alkynes succeeded to give phosphirenes when complex **5** was not detected in the performed DFT study. One possible explanation is that the accuracy of the formalism was not high enough to detect the local minimum corresponding to allylphosphinidene complex **5**.

After DFT study, the thermolysis of phosphanorbornadiene complex **4** was re-investigated and complexes **6a**, **6b** and **8** were reproducibly obtained (Scheme 2.5) and unambiguously characterised by single x-ray crystallography.

Scheme 2.5 Thermolysis of 7-allyl-7-phosphanorbornadiene complex **4**

Complexes **6a** and **6b** are undoubtedly head-to-tail dimerisation products (Scheme 2.6). Even though these complexes have been partially characterised by NMR and mass spectra in the previous work,¹⁶ the structures were not fully confirmed then.

Scheme 2.6 Head-to-tail dimerisation of allylphosphinidene complex **5**

Stereoisomers **6a** and **6b** are similar as far as NMR parameters are concerned. Both have characteristic high-field shifts: $\delta^{31\text{P}}$ -198.6 for **6a** and -182.8 for **6b**, as expected from three-membered phosphacycles. The molecular structure of **6a** (Fig. 2.3) consists of a quasiplanar six-

membered ring with one fused three-membered ring facing upwards and another fused-ring facing downwards.

Figure 2.3 X-ray crystal structure of stereoisomer **6a**. Selected distances (Å) and angles (deg.): P-W 2.486(4), P-C6 1.814(5), P-C7 1.862(5), P-C8 1.825(5), C6-C7 1.494(7), C7-C8 1.523(7); C6-P-C7 47.9(2), C6-P-C8 105.8(3), C8-C7-P 128.6(4), C6-C7-C8 120.7(5), C6-C7-P 64.4(3).

However, interestingly, the molecular structure of **6b** (Fig. 2.4) displays a W shape. The central six-membered ring is bent around C13-C16 axis with the two planes forming an angle of 57.6°. The two fused three-membered rings are facing up with an angle of 74.2° formed between the fused rings and the vicinal planes of the six-membered ring.

Figure 2.4 X-ray crystal structure of stereoisomer **6b**. Selected distances (Å) and angles (deg.): P-W 2.492(4), P-C11 1.831(15), P-C12 1.852(14), P-C16 1.846(14), C11-C12 1.531(18), C15-C16 1.500(19); C11-P-C12 49.1(6), C11-P-C16 106.7(7), C15-C16-P 112.2(9), C11-C12-C13 119.9(12), C11-C12-P 64.7(7).

Meanwhile, the novel dimer **8** ($\delta^{31}\text{P}$ -6.1 and 21.1, $^1J_{\text{PP}}$ = 164.7 Hz) is a totally unforeseen product from the thermolysis reaction of phosphanorbornadiene **4**. The molecular structure of dimer **8** is made up of two fused five-membered rings with phosphorus atoms at ring junctions (Fig. 2.5). The two fused-rings are almost perpendicular to each other (84.9°) and the distance between two phosphorus atoms lies within the range of P-P bond length.

Figure 2.5 X-ray crystal structure of dimer **8**. Selected distances (Å) and angles (deg.): P1-P2 2.2306(19), P1-W1 2.4850(14), P2-W2 2.5003(13), P1-C11 1.829(12), C11-C12 1.51(3), C12-C13 1.51(2), C13-P2 1.863(10), P2-C14 1.836(12), C14-C15 1.43(2), C15-C16 1.37(3), C16-P1 1.826(11); P1-P2-W2 129.38(7), P2-P1-W1 125.57(7), P1-P2-C13 91.7(7), P1-P2-C14 94.7(8), C13-P2-C14 103.5(9), P2-P1-C11 93.8(12), P2-P1-C16 93.2(13), C11-P1-C16 103.8(11).

Scheme 2.7 Isomerisation of allylphosphinidene complex **5** into 1-phosphabutadiene complex **9**

It is proposed that the reaction is set off by isomerisation of allylphosphinidene complex **5** into 1-phosphabutadiene complex **9** (Scheme 2.7). Once the isomerisation takes place, the two structural isomers react to give [4+1] cycloadduct **10**. Ring-closing of **10** by intramolecular hydrophosphination consequently gives dimer **8**.

Scheme 2.8 Proposed mechanism for the formation of dimer **8**

Although a [1,2] hydrogen shift from carbon to phosphorus has not been seen in the literature previously, it is common for alkylcarbenes to undergo [1,2] migration of hydrogen to afford alkenes and the barrier to such rearrangement can often be negligible.^{21, 22} Like other electrophilic phosphinidene complexes, allylphosphinidene complex **5** is predicted to be isolobal with allylcarbene since the phosphorus in complex **5** is shown to be electrophilic, bearing a considerably high positive charge, by DFT computation presented earlier. Meanwhile, theoretical study on the activation energy for a [1,2] hydrogen shifts in substituted methylcarbenes has been carried out at several different levels of theory by Houk and co-worker and the calculations predicted that the activation barrier for such migration in allylcarbene is the lowest compared to methylchlorocarbene, methylhydroxycarbene and methylmethoxycarbene.²³ Therefore, it is not impossible that allylphosphinidene complex **5** would isomerise into 1-phosphabutadiene complex **9**. In fact, DFT study at B3PW91/6-31G(d)-Lanl2dz (W) level indicates that the diene **9** is more stable than adduct **7** by 175.8 kcal mol⁻¹.²⁰

Besides, the reactivity of 1-phosphabutadienes has already been explored and some derivatives of 1-phosphabutadiene exhibit ambident reactivity, behaving as both diene and dienophile, and dimerise in [4+2] cycloaddition mode (Scheme 2.9).²⁴⁻²⁶ Moreover, the transient 1-phosphabutadiene complexes have been shown to react with various dienophiles such as *N*-phenylmaleimide, dimethyl acetylenedicarboxylate and benzaldehyde to give [4+2] cycloadducts (Scheme 2.10).^{27, 28} These experimental results are supported by an ab initio study performed by Bachrach, revealing favorable energetics for the Diels-Alder reactions of phosphabutadienes. The activation energy for the Diels-Alder reaction of ethene with 1-phosphabutadiene has been

calculated at the MP2 level to be less than 20 kcal mol⁻¹.²⁹ Hence, 1-phosphabutadiene complex **9** can act as a reactive diene and perform cycloaddition with phosphinidene complex **5**.

Scheme 2.9 Dimerisation of 1-phosphabutadienes

Scheme 2.10 Reaction of 1-phosphabutadiene complex with *N*-phenylmaleimide and benzaldehyde

Conventionally, olefin hydrophosphination is a radical or base promoted reaction. Yet, intramolecular hydrophosphination in the absence of a base or radical initiator is not unprecedented. Reaction of a Cp* substituted phosphinidene of the type [Cp*P(W(CO)₅)₂] with two equivalents of primary phosphine Cp*PH₂ to produce triphosphine involves intramolecular hydrophosphination in the reaction pathway (Scheme 2.11).³⁰ In addition, it has been discovered that when a phosphine oxide is directly bonded to an unsaturated group, the P-H bond of phosphine oxide is activated and the hydrophosphination reaction with *N*-benzylidenemethylamine can proceed uncatalysed at room temperature (Scheme 2.12).³¹ Likewise, intramolecular hydrophosphination of compound **10** is anticipated to take place yielding the ring-closing product **8**.

Scheme 2.11 Reaction of Cp* substituted phosphinidene complex with Cp*PH₂

Scheme 2.12 Hydrophosphination of vinylphosphine oxide with *N*-benzylidenemethylamine

With such backgrounds, the earlier presented mechanism for the formation of dimer **8** (Scheme 2.8) seems feasible. However, since the thermal fragmentation of 7-allyl-7-phosphanorbornadiene complex **4** does not give the expected 1-phosphabicyclo[1.1.0]butane complex, the investigation on the effect of increasing angle strain on phosphirane comes to an abrupt stop. Moving on to enquire on the potential role of the additional steric strain in phosphirane chemistry, the *exo* products from condensing phosphinidene complex to norbornene serve as ideal systems to start with. The results are reported herein.

Scheme 2.13 Cycloaddition of methylphosphinidene complex to norbornene

Methylphosphinidene complex, generated in-situ from thermal fragmentation of 7-methyl-7-phosphanorbornadiene complex **11**, readily reacts with norbornene to give phosphirane

complexes **12** and **13** with 65% overall yield (Scheme 2.13). Only formation of *exo* phosphiranes is observed from the condensation: *syn* isomer **12** and *anti* isomer **13**, with the *anti* isomer as the major product. ^{31}P NMR shifts of isomers **12** and **13** are extremely high-field ($\delta^{31}\text{P}$ for -194.0 for **12** and -170.2 for **13**). NMR parameters of **12** and **13** are considerably similar to those of cycloadducts reported in an earlier work by the Lammertsma group.¹⁵ The molecular structures have been established by single crystal X-ray analysis (Fig. 2.6 and 2.7). The formation of the thermodynamically stable *exo* adducts is purely due to steric reason: the *exo* face is less hindered.

Figure 2.6 X-ray crystal structure of *syn* phosphirane complex **12**. Selected distances (Å) and angles (deg.): P-W 2.5224(9), P-C6 1.823(3), P-C7 1.831(3), P-C8 1.834(3), C7-C8 1.562(5); Me-P-C7 101.69(16), C7-P-C8 50.46(15), C12-C7-P 122.1(2), C13-C12-C7 103.2(3).

Looking at the molecular geometry of complexes **12** and **13**, the intriguing question arises whether the norbornane CH_2 bridge affects the annulated phosphirane. Structures of **12** and **13** were then computed by DFT at the B3PW91/6-31G(d)-LanI2dz (W) level.²⁰ The calculated structural parameters are in agreement with the X-ray structures. It is noteworthy that the *syn* isomer is computed to be more stable than the *anti* isomer by 4.4 kcal mol⁻¹ (by comparing the ground state energy minimizations of **12** and **13**).

Figure 2.7 X-ray crystal structure of *anti* phosphirane complex **13**. Selected distances (Å) and angles (deg.): P-W 2.5038(13), P-C6 1.829(5), P-C7 1.845(10), P-C8 1.830(9), C7-C8 1.535(12); Me-P-C7 118.0(6), C7-P-C8 49.4(4), C11-C7-P 126.7(11), C10-C11-C7 104.2(9).

For comparison, DFT calculations have also been performed on uncomplexed phosphiranes **14** and **15** at the B3PW91/6-311+G(d,p) level.²⁰ Several significant differences between structures of **14** and **15** are noted, which relate to the steric repulsion between the norbornane CH₂ bridge and the annulated phosphirane ring. In the *anti* isomer **14** (Fig. 2.8), the Me-P/phosphirane plane angle is computed to be 93.9°. However, that corresponding angle increases to 100.4° in the *syn* isomer **15** (Fig. 2.9). In agreement with this observation, the angle between bridge plane and junction plane of norbornane increases from 127.5° for the *anti* isomer **14** to 130° for the *syn* isomer **15**, highlighting the effect of repulsion by the P-Me group on the norbornane bridge in the *syn* isomer **15**. Whereas the HOMO which correlates to the phosphorus lone pair is not affected by this distortion (*anti*: -6.50 eV and *syn*: -6.48 eV), the LUMO of the *anti* isomer **14** (+0.30 eV) is higher in energy than that of the *syn* isomer **15** (+0.11 eV). All in all, the steric repulsion destabilises the *syn* isomer **15** by 7.7 kcal mol⁻¹, compared to *anti* isomer **14**, since the difference in their ground state energy minimizations is 7.7 kcal mol⁻¹.

Figure 2.8 Computed structure of *anti* phosphirane **14**. Selected distances (Å) and angles (deg.): P-C19 1.862, P-C14 1.867, C12-C14 1.513; Me-P-C14 98.6, C12-P-C14 47.8, C3-C14-P 119.3, C14-C3-C9 102.6.

Meanwhile, when the phosphirane/junction interplane angle is examined, the similarity between the *anti*-**13** and *syn*-**15** is noted (126.3° in **15** vs. 125.3° in **13**). Hence, the steric strain is postulated to be identical for **13** and **15**. This is in contrast with the other pair, **12** and **14**. Upon complexation, there is an increase of that folding angle between the phosphirane plane and the norbornane junction plane (116.0° in **14** vs. 120.2° in **12**). From this standpoint, if destabilisation by steric strain for **13** and **15** is admitted to be identical, then *syn*-**12** is destabilised by complexation by $3.3 \text{ kcal mol}^{-1}$ (Fig. 2.10). The release of this strain can facilitate the demetallation of complex **12**.

Moreover, recalling from DFT study on the free phosphiranes, the LUMO energy of *anti*-**14** is higher than that of *syn*-**15**, indicating that *anti*-**14** is a weaker acceptor. This theoretical prediction is corroborated by the longer P-W bond distance observed in the *syn* complex ($2.5224(9) \text{ Å}$ in **12** vs. $2.4983(14) \text{ Å}$ in **13**).

Figure 2.9 Computed structure of *syn* phosphirane **15**. Selected distances (Å) and angles (deg.): P-C19 1.868, P-C14 1.863, C12-C14 1.521; Me-P-C14 112.1, C12-P-C14 48.1, C3-C14-P 128.6, C14-C3-C9 104.1.

Figure 2.10 Computed stabilisation energy from DFT studies

Initial recovery attempts of **14** and **15** from **12** and **13**, respectively, by classical decomplexation method with 1,2-bis(diphenylphosphino)ethane was not successful. Complete decomposition was noticed from the reaction. Interestingly, applying the milder decomplexation technique by using carbon monoxide, only *syn* phosphirane **12** is decomplexed. Under CO

pressure, the W(CO)_5 fragment detaches from the P of *syn* phosphirane **12** by CO substitution yielding compound **14** ($\delta^{31}\text{P}$ -240.9) whereas *anti* isomer **13** is recovered at the end of the reaction (Scheme 2.14). This selective decomplexation further substantiates the influence of steric strain.

Scheme 2.14 Selective decomplexation by carbon monoxide

Compared to other phosphines, phosphiranes can behave as better π -acceptors due to their strong pyramidalisation of the phosphorus coordination sphere.³² Hence, ordinary phosphiranes are known to coordinate to transition metals, other than tungsten and molybdenum, to give stable complexes.³³⁻³⁶ However, phosphirane **14** is discovered to be a poor ligand since stirring of **14** with Pd(OAc)_2 , $\text{Rh(CO)}_2(\text{acac})$ or RuCl_3 at room temperature led to decomposition and no reaction took place with $\text{Pd}_2(\text{dba})_3$.

Another intriguing phenomenon was discovered, which can be related to the effect of steric strain in the system. Palladium acetate was found to perform stoichiometric oxidative cleavage of phosphirane complexes **12** and **13** yielding phosphine complex **16** with a ^{31}P NMR resonance at 165.8 ppm (Scheme 2.15). Generally, phosphiranes tend to form metallaphosphetanes with Pd(0) via insertion of the metal into one of intracyclic the P-C bonds.^{37, 38} Although this kind of chemistry has not been seen with Pd(II) , it does not lead to the complete disruption of the ring.

Scheme 2.15 Stoichiometric reaction of palladium acetate with coordinated phosphiranes

A reaction mechanism is proposed involving an insertion of Pd into the P-C bond of phosphirane ring at the onset of the reaction (Scheme 2.16). This insertion is favored by the additional strain induced in the phosphirane ring upon annulation with norbornane. Next, intramolecular nucleophilic reaction occurs, followed by insertion of Pd into another P-C bond destabilised by the steric repulsion of the methylene bridge. A mechanism involving a redox reaction of palladium acetate with methylphosphinidene complex is excluded because the reaction takes place at room temperature while much higher temperature is required to generate methylphosphinidene complex from the phosphiranes. The reaction depicted in scheme 2.15 is further supported by the fact that reacting a phosphirane annulated with cyclohexane with palladium acetate does not give phosphine **16** in any significant amount under the same reaction conditions.

Scheme 2.16 Proposed mechanism for formation of phosphine **16**

2.3 Conclusion

Phosphiranes are well-known for their unique reactivities owing to their inherent strain. Thus, the potential effects of additional strain on the chemistry of phosphiranes are explored in this chapter. The first objective is to study the influence of the extra angle strain present in 1-phospha-bicyclo[1.1.0]butane. Taking into consideration the formation of 1-phospha-bicyclo[3.1.0]hexane complex **3** from the self-condensation of pentenylphosphinidene complex **2**, the self-condensation of allylphosphinidene complex **5** could potentially generate 1-phospha-bicyclo[1.1.0]butane complex. However, only dimers **6** and **8** were isolated and characterised from the thermolysis of 7-allyl-7-phosphanorbornadiene complex **4**.

Consequently, it was decided to proceed with the investigation on the potential role of additional steric strain present in norbornane-annulated phosphirane complexes **12** and **13**. The steric repulsion induced by the norbornane methylene bridge on the phosphirane leads to a number of structural distortions, especially the interplane angles. When both complexes **12** and **13** were subjected to CO pressure in boiling toluene, only selective decomplexation of **12** to free phosphirane **14** was observed. Furthermore, when phosphiranes **12** and **13** were stirred with palladium acetate at room temperature, an unexpected stoichiometric oxidative cleavage took place to give phosphine **16**. It is postulated that these observed interesting reaction behaviours of phosphiranes **12** and **13** are observed due to the role of steric strain present in the system.

2.4 Experimental

All reactions were carried out under nitrogen with distilled dry solvents. All commercially available reagents were used as received from the suppliers unless otherwise specified. Silica gel (230-400 mesh) was used for the chromatographic separations. Cold column chromatography is performed on a jacketed column where low temperature is maintained by a constant flow of chilled solution mixture of water and ethylene glycol. NMR spectra were recorded on either a Bruker BBFO 400 MHz or JEOL ECA 400 spectrometer. All spectra were recorded at 298K. Proton decoupling was applied for ^{13}C and ^{31}P spectra. HRMS were obtained on a Water Q-ToF Premier MS. X-ray crystallographic analyses were performed on a Bruker X8 APEX CCD diffractometer or a Bruker Kappa CCD diffractometer. Reactions with CO were performed inside a glass liner in a *Parr Instrument Co.* 4560 Mini Bench Top Reactor, using a *Parr Instrument Co.* 4848 Reactor Controller.

Thermolysis of (7-allyl-7-phosphanorbornadiene)pentacarbonyltungsten 4

Compound **4** (1.0 g, 1.62 mmol) in 8 ml of toluene was stirred in a pressure tube at 110°C for 24 h. The reaction mixture was evaporated under vacuum and the black residue was chromatographed on silica gel to give **6a**, **6b** and **8**.

(1,5-diphosphatricyclo[5.1.0.0^{3,5}]octane)decacarbonylditungsten (6a,b)

Compound **6a** was eluted from column chromatography with hexane/ethyl acetate 90:10 and recrystallized from hexane/ethyl acetate to yield 77 mg (12%) of colorless crystals; ³¹P NMR (CD₂Cl₂) δ -198.6 (¹J_{PW} = 260.1 Hz); ¹H NMR (CD₂Cl₂) δ 1.51 (m, 4H, CH₂), 1.59 (m, 2H, CH), 2.31 (m, 2H, CH₂), 2.73 (m, 2H, CH₂); ¹³C NMR (CD₂Cl₂) δ 12.06 (t, ¹J_{CP} ≈ 12 Hz, CH), 14.24 (d, ¹J_{CP} ≈ 5.7 Hz, CH₂), 23.51 (pseudo-t, ¹J_{CP} ≈ 9 Hz, CH₂), 195.99 (pseudo-t, ²J_{CP} ≈ 9.5 Hz, *cis* CO), 198.12 (pseudo-t, ²J_{CP} ≈ 31 Hz, *trans* CO); MS (*m/z*, relative intensity) 814.8648 (calcd for C₁₆H₁₀O₁₀P₂W₂Na 814.8666).

Compound **6b** was eluted with hexane/ethyl acetate 75:25 and recrystallized from hexane/ethyl acetate giving 60 mg (9.3%) of colorless crystals; ³¹P NMR (CDCl₃) δ -182.8 (¹J_{PW} = 262.2 Hz); ¹H NMR (CDCl₃) δ 1.08 (m, 2H, CH₂), 1.31 (d, ²J_{HP} = 6.1 Hz, 2H, CH₂), 1.64 (pseudo-t, ²J_{HP} = 18.2 Hz, 2H, CH₂), 1.97 (t, ²J_{HP} = 7.8 Hz, 2H, CH), 2.97 (m, 2H, CH₂); ¹³C NMR (CDCl₃) δ 16.32 (t, ¹J_{CP} = 6.6 Hz, CH), 23.60 (d, ¹J_{CP} = 6.5 Hz, CH₂), 30.05 (t, ¹J_{CP} = 6.5 Hz, CH₂), 195.30 (pseudo-t, ²J_{CP} = 7.7 Hz, *cis* CO), 197.25 (pseudo-t, ²J_{CP} = 32 Hz, *trans* CO); MS (*m/z*, relative intensity) 814.8665 (calcd for C₁₆H₁₀O₁₀P₂W₂Na 814.8666).

(1,5-diphosphabicyclo[3.3.0]oct-3-ene)decacarbonyl tungsten (8)

Compound **8** was eluted with hexane/ethyl acetate 80:20. Recrystallization from hexane/ethyl acetate yielded 114 mg (17.8 %) of light brown crystals; ^{31}P NMR (CD_2Cl_2) δ 21.1, -6.1 ($^1J_{\text{PP}} = 164.7$ Hz, $^1J_{\text{PW}} = 234.0$ and 234.1 Hz); ^1H NMR (CD_2Cl_2) δ 1.64 (m, 1H, CH_2), 1.96 (t, $^2J_{\text{HP}} = 14$ Hz, 1H, CH_2), 2.09 (t, $^2J_{\text{HP}} = 14$ Hz, 1H, CH_2), 2.33 (m, 1H, CH_2), 2.41 (m, 1H, CH_2), 2.45 (m, 1H, CH_2), 3.31 (m, 2H, CH_2), 6.04 (dt, $^2J_{\text{HP}} = 34$ Hz, $^3J_{\text{HP}} = 8.7$ Hz, 1H, CH), 6.54 (m, 1H, CH); ^{13}C NMR (CD_2Cl_2) δ 28.12 (pseudo-t, $^1J_{\text{CP}} \approx 11$ Hz, CH_2), 38.40 (dd, $^1J_{\text{CP}} \approx 12$ Hz, $^2J_{\text{CP}} \approx 4$ Hz, CH_2), 40.68 (dd, $^1J_{\text{CP}} \approx 12$ Hz, $^2J_{\text{CP}} \approx 3$ Hz, CH_2), 45.61 (dd, $^1J_{\text{CP}} \approx 11$ Hz, $^2J_{\text{CP}} \approx 4$ Hz, CH_2), 130.01 (dd, $^1J_{\text{CP}} = 19.4$ Hz, $^2J_{\text{CP}} = 5.8$ Hz, CH), 144.39 (d, $^2J_{\text{CP}} = 6$ Hz, CH), 196.48 (d, $^2J_{\text{CP}} = 7.5$ Hz, *cis* CO), 196.58 (d, $^2J_{\text{CP}} = 6.5$ Hz, *cis* CO), 198.78 (d, $^2J_{\text{CP}} = 25$ Hz, *trans* CO), 199.03 (d, $^2J_{\text{CP}} = 25$ Hz, *trans* CO); MS (m/z , relative intensity) 814.8651 (calcd for $\text{C}_{16}\text{H}_{10}\text{O}_{10}\text{P}_2\text{W}_2\text{Na}$ 814.8666).

(3-methyl-3-phosphatricyclo[3.2.1.0^{2,4}]octane)pentacarbonyl tungsten (12,13)

(7-methyl-7-phosphanorbornadiene)pentacarbonyl tungsten **11** (1 g, 1.69 mmol) was stirred with norbornene (0.955 g, 10.14 mmol) in toluene at 120°C for 24 h. After evaporation of the solvent, the residue was purified by cold column chromatography on silica gel -10°C using hexane as the eluent, yielding of a mixture of products **12** and **13**. A second silica chromatography at -10°C was carried out to separate the two isomers with hexane as the eluent. The *syn* isomer **12** was first eluted out from the column (221.7 mg, 28.3%). The *anti* isomer **13** was then recovered (288.3 mg, 36.74%).

Compound **12**: ^{31}P NMR (CD_2Cl_2) δ -194.0 (s, $^1J_{\text{PW}} = 251.4$ Hz); ^1H NMR (CDCl_3) δ 0.94 (dt, 1H, $^2J_{\text{HH}} = 11.0$ Hz, $^4J_{\text{HH}} = 1.4$ Hz, $\text{CH}_2(\text{syn})$), 1.81 (d, 1H, $^2J_{\text{HH}} = 11.0$ Hz, $\text{CH}_2(\text{anti})$), 1.22 (d, 3H, $^2J_{\text{PH}} = 5.5$ Hz, CH_3), 1.31 (s, 2H, PCH), 1.36 (dd, 2H, $^2J_{\text{HH}} = 7.3$ Hz, $^4J_{\text{HH}} = 2.3$ Hz, $\text{CH}_2(\text{endo})$), 1.62 (d, $^2J_{\text{HH}} = 6.9$ Hz, 2H, $\text{CH}_2(\text{exo})$), 2.68 (s, 2H, CH); ^{13}C NMR (CD_2Cl_2) δ 18.6 (d, $^1J_{\text{CP}} = 21$ Hz, CH_3), 28.8 (d, $^1J_{\text{CP}} = 8.6$ Hz, CHP), 31.3 (d, $^3J_{\text{CP}} = 7.6$ Hz, CH_2CH_2), 32.8 (d, $^3J_{\text{CP}} = 15.3$ Hz, CH_2 bridge), 37.6 (s, CH), 196.9 (d, $^2J_{\text{CP}} = 8.6$ Hz, cis CO), 199.3 (d, $^2J_{\text{CP}} = 30.6$ Hz, trans CO); MS (m/z , relative intensity) 464.0012 (calcd for $\text{C}_{13}\text{H}_{13}\text{O}_5\text{PW}$ 464.0010).

Compound **13**: ^{31}P NMR (CD_2Cl_2) δ -170.2 (s, $^1J_{\text{PW}} = 255.8$ Hz); ^1H NMR (CD_2Cl_2) δ 0.97 (d, 1H, $^2J_{\text{HH}} = 11.3$ Hz, $\text{CH}_2(\text{anti})$), 1.08 (dt, 1H, $^2J_{\text{HH}} = 11.3$ Hz, $^4J_{\text{HH}} = 1.8$ Hz, $\text{CH}_2(\text{syn})$), 1.39 (dd, 2H, $^2J_{\text{HH}} = 7.7$ Hz, $^4J_{\text{HH}} = 2.3$ Hz, $\text{CH}_2(\text{endo})$), 1.48 (d, 2H, $^2J_{\text{HH}} = 10.9$ Hz, PCH), 1.67 (d, 2H, $^2J_{\text{HH}} = 7.2$ Hz, $\text{CH}_2(\text{exo})$), 1.70 (d, 3H, $^2J_{\text{PH}} = 5.0$ Hz, CH_3), 2.85 (s, 2H, CH); ^{13}C NMR (CD_2Cl_2) δ 13.3 (d, $^1J_{\text{CP}} = 4.8$ Hz, CH_3), 31.1 (d, $^3J_{\text{CP}} = 9.5$ Hz, CH_2 bridge), 31.7 (d, $^1J_{\text{CP}} = 12.4$ Hz, CHP), 32.6 (d, $^3J_{\text{CP}} = 3.9$ Hz, CH_2CH_2), 39.6 (d, $^2J_{\text{CP}} = 7.6$ Hz, CH), 197.2 (d, $^2J_{\text{CP}} = 8.6$ Hz, cis CO), 199.6 (d, $^2J_{\text{CP}} = 27.7$ Hz, trans CO); MS (m/z , relative intensity) 464.0012 (calcd for $\text{C}_{13}\text{H}_{13}\text{O}_5\text{PW}$ 464.0010).

3-methyl-3-phosphatricyclo[3.2.1.0^{2,4}]octane (**14**)

Complex **12** (100 mg, 0.216 mmol) was stirred under CO (50 bar) in toluene at 120°C for 16 h in a high pressure reactor. ^{31}P NMR (CDCl_3) δ -240.9; ^1H NMR (CDCl_3) δ 0.44 (d, 3H, $^2J_{\text{PH}} = 5.7$ Hz, CH_3), 0.64 (dm, 1H, $^2J_{\text{HH}} = 12.0$ Hz, $\text{CH}_2(\text{syn})$), 1.02 (d, 1H, $\text{CH}_2(\text{anti})$), 1.18 (s, 2H, PCH), 1.33 (dd, 2H, $^2J_{\text{HH}} = 7.2$ Hz, $^4J_{\text{HH}} = 2.2$ Hz, $\text{CH}_2(\text{endo})$), 1.51 (d, $^2J_{\text{HH}} = 7.1$ Hz, 2H, $\text{CH}_2(\text{exo})$), 2.46 (s, 2H, CH); ^{13}C NMR (CDCl_3) δ 8.70 (d, $^1J_{\text{CP}} = 30.8$ Hz, CH_3), 30.4 (s, CH_2CH_2), 30.5 (d, $^1J_{\text{CP}} = 37.1$ Hz, CHP), 31.2 (d, $^3J_{\text{CP}} = 29.4$ Hz, CH_2 bridge), 38.3 (d, $^2J_{\text{CP}} = 7.8$ Hz, CH); MS (m/z , relative intensity) 163.0653 (calcd for $\text{C}_8\text{H}_{13}\text{PNa}$ 163.0653).

(diacetate(methyl)phosphine)pentacarbonyltungsten (16)

Phosphiranes **12** and **13** (50 mg, 0.108 mmol) were reacted with $\text{Pd}(\text{OAc})_2$ (24 mg, 0.108 mmol) in THF at RT for 3 h. After solvent evaporation, the residue was purified by cold column chromatography on silica gel using 1:1 hexane/dichloromethane as the eluent, yielding 20 mg (38 %) of **16**. ^{31}P NMR (CDCl_3) δ 165.8 ($^1J_{\text{PW}} = 338.1$ Hz); ^1H NMR (CDCl_3) δ 2.23 (d, 6H, $^4J_{\text{PH}} = 1.37$ Hz, CH_3), 2.32 (d, 3H, $^2J_{\text{PH}} = 3.2$ Hz, CH_3); ^{13}C NMR (CDCl_3) δ 22.4 (s, OCH_3), 28.2 (d, $^1J_{\text{CP}} = 26.9$, CH_3), 167.5 (d, $^2J_{\text{CP}} = 6.7$ Hz, $\text{C}=\text{O}$), 195.1 (d, $^2J_{\text{CP}} = 8.6$ Hz, cis CO), 198.2 (d, $^2J_{\text{CP}} = 37.3$ Hz, trans CO); MS (m/z , relative intensity) 487.9496 (calcd for $\text{C}_{13}\text{H}_{13}\text{O}_5\text{PW}$ 487.9494).

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3.1 Introduction

1-chlorophosphiranes can be prepared by several different approaches,¹⁻⁴ which have been reviewed in the first chapter of this dissertation. It is necessary to introduce bulky substituents, such as trimethylsilyl group, on the respective ring carbons for stabilisation against ring-opening. Nevertheless, unsubstituted 1-chlorophosphirane is known and it has been successfully isolated at -80°C.⁵ Due to its instability, it is stored as complexes of tungsten and chromium carbonyls. Generally, 1-chlorophosphirane complexes are assembled within the metal coordination sphere from the acyclic precursors, taking advantage of the stabilising effect of those transition metals.⁶⁻⁸

The chemical reactivity of *P*-chlorine-substituted phosphiranes has been fairly investigated. Treatment of 1-chlorophosphiranes, either in the free state or as complexes, with nucleophiles allows substitution of the chlorine atom and generates a wide range of *P*-substituted phosphiranes.^{1, 3, 6-9} However, excess of nucleophiles would induce ring fragmentation to give alkenes and oligophosphines; hence extra caution is imperative. On the contrary, the heavily substituted 1-chlorophosphirane **17** is resistant to strong alkylating reagent such as methyl iodide and methyl triflate.³ Surprisingly, attempts to obtain phosphiranylium ion **18** from phosphirane **17** resulted in the curious rearrangement product **19**. It is hypothesized that the chloride abstraction from phosphirane **17** by aluminium trichloride is spontaneously followed by an intramolecular atom-exchange to give Lewis acid-base adduct **19** (Scheme 3.1).³ Anyhow, this reaction is the only example of interaction between 1-chlorophosphirane and a Lewis acid found in the literature.

So far, neither parent phosphiranylium ion $[\text{C}_2\text{H}_4\text{P}]^+$ nor its substituted derivatives have been isolated yet. Such a phosphiranyl cation has nonetheless been theoretically investigated. One computational study predicts the electrocyclic ring opening into 2-phosphaallyl cation to be

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difficult since the open-chain cation is less stable.¹⁰ Another suggests an easy disrotatory ring opening into the bis(methylene)phosphorane cation.¹¹

Scheme 3.1 Chloride abstraction of substituted 1-chlorophosphirane by AlCl_3 followed by intramolecular atom-exchange

Very recently, Lammertsma has reported the *N*-alkylated BABAR-Phos **21** as an intramolecular amine complex of phosphiranylium ion **22** (Scheme 3.2).¹² Likewise, compound **24** is viewed as an intermolecular carbene-stabilised phosphiranyl cation. These may be regarded as the first isolated stabilised-phosphiranylium ions.

Scheme 3.2 Preparation of amino- and carbene-stabilised phosphiranylium ions

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By comparison, aluminium trichloride readily reacts with 1-chlorophosphirene complex **25** in dichloromethane to give the expected phosphirenylium ion **26** (Scheme 3.3).¹³ The 2π Hückel aromatic cation is said to be stable in dichloromethane solution but rapidly decomposes upon recrystallisation.

Scheme 3.3 Chloride abstraction of 1-chlorophosphirene complex by AlCl_3

In fact, another phosphirenylium ion has been prepared earlier by Regitz et al. The addition of the powerful Lewis acid $\text{B}(\text{OTf})_3$ to a *P*-triflate-substituted phosphirane in liquid SO_2 led to triflate abstraction.¹⁴ Detailed investigations on the electronic properties and particularly on the aromatic character of the phosphirenylium ion have been carried out by means of computational studies, which revealed that the aromatization helps to stabilise the corresponding cation.¹⁴⁻¹⁷

Therefore, it is of particular interest to further probe the interaction of the 1-chlorophosphirane complex with a strong Lewis acid such as aluminium trichloride, which may potentially extend the versatility of 1-chlorophosphirane. A detailed account of this study is reported in this chapter.

3.2 Results and Discussion

The recent availability of transient chlorophosphinidene complex **27** has provided a convenient access to 1-chlorophosphirane complexes **28** by condensing **27** with alkenes (Scheme 3.4).⁸

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Scheme 3.4 Condensation reaction of chlorophosphinidene **27** with alkene

However, 7-chloro-7-phosphanorbornadiene complex **30**, which is the precursor of phosphinidene **27**, is too reactive to be isolated in good yield (Scheme 3.5).

Scheme 3.5 Synthesis of 7-chloro-7-phosphanorbornadiene complex **30**

Consequently, the condensation reaction of phosphinidene **27** with cyclohexene to give the annulated chlorophosphirane **31** is carried out in a one-pot reaction of 1-chlorophosphole complex **29**, dimethyl acetylenedicarboxylate and cyclohexene (Scheme 3.6).⁸

Scheme 3.6 Synthesis of 1-chlorophosphirane complex **31**

When 1-chlorophosphirane complex **31** was treated with aluminium trichloride in dichloromethane, ^{31}P NMR spectrum of the resulting product showed a single phosphorus resonance at 162.9 ppm, deshielded by 226 ppm from the precursor. Obviously, ring cleavage of the three-membered ring has occurred since the characteristic high-field ^{31}P resonance of phosphirane was not observed in the recorded spectrum. Deducing from the ^1H and ^{13}C NMR

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spectra as well as the high-resolution mass spectrum, the structure of the ring-cleavage product was established as dichloro(cyclohexyl)phosphine complex **32**. However, no suitable crystals for X-ray structure analysis could be obtained even after multiple attempts of recrystallisation. Therefore, another method was sought to confirm the identity of phosphine **32**. This phosphine was successfully reproduced from the reaction of $W(CO)_5$ complex of phosphorus trichloride with cyclohexylmagnesium bromide in tetrahydrofuran.

The formation of phosphine **32** from chlorophosphirane **31** can only be rationalised as phosphorus-carbon bond cleavage by hydrogen chloride, which contaminates aluminium trichloride (Scheme 3.7). But, 1-chlorophosphirane tungsten complex is known to be stable in the presence of hydrogen chloride.⁶ This thus implies that aluminium trichloride catalyses the ring-opening of phosphirane **31** by hydrogen chloride.

Scheme 3.7 Ring cleavage of chlorophosphirane **31** catalysed by aluminium trichloride

Meanwhile, reaction of chlorophosphirane **31** with aluminium trichloride and thiophene in dichloromethane gives 2-thienyl-substituted phosphirane **33** ($\delta^{31}\text{P}$ -171.5). This result is unsurprising since aluminium trichloride is a well-known catalyst for Friedel-Crafts alkylation of aromatic rings. Though Friedel-Crafts reactions sometimes require stoichiometric quantities of aluminium trichloride, the necessity for a huge excess of the Lewis acid (i.e. 6 equivalents) in this substitution reaction is unusual (Scheme 3.8). This puzzling issue will be addressed later.

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Scheme 3.8 AlCl_3 -catalysed electrophilic aromatic substitution of thiophene

The x-ray crystal structure of 1-(2-thienyl)phosphirane complex **33** (Fig. 3.1) shows that the tungsten carbonyl group is facing the cyclohexane ring, similar to the geometrical structure of 1-chlorophosphirane complex **31**.⁸ Hence, this indicates that the stereochemistry of phosphorus is preserved during the substitution reaction.

Figure 3.1. X-ray crystal structure of phosphirane **33**. Selected distances (Å) and angles (deg.): P1-W1 2.5078(9), P1-C6 1.803(4), P1-C10 1.841(4), P1-C11 1.849(4), C6-S1 1.724(4), C9-S1 1.718(4), C6-C7 1.370(5), C7-C8 1.418(6), C8-C9 1.348(6), C10-C11 1.520(5); C10-P1-C11 48.64(17), C10-P1-C6 102.75(17), C11-P1-C6 105.43(17), C6P1-W1 116.83(12).

In order to fully understand the role of aluminium trichloride in the reaction, DFT study was performed at the B3LYP/6-31G(d)-Lanl2dz(W) level to study the interaction between

aluminium trichloride and the unsubstituted 1-chlorophosphirane tungsten complex **34**.¹⁸ The computed structural parameters of **34** (Fig. 3.2) are consistent with the X-ray crystal structure obtained in a previous work.⁶

Figure 3.2 Computed structure of unsubstituted 1-chlorophosphirane complex **34**. Selected distances (Å) and angles (deg.): P8-W19 2.512, P8-Cl7 2.092, P8-C1 1.838; C1-P8-C2 48.96, Cl7-P8-C1 103.62, C1-P8-W19 129.56, Cl7-P8-W19 120.59.

Optimisation of the **34**-AlCl₃ system resulted in the loose complex **35** in which AlCl₃ interacts with the chlorine atom of **34** (Fig. 3.3). Whereas the structures of the phosphirane ring in both **34** and **35** are considerably alike, an increasing bond length of P-Cl from 2.092 to 2.216 Å is observed upon complexation with AlCl₃. It is important to note that the Al...Cl interaction is loose (2.479 vs. 2.107-2.123 Å for the normal Al-Cl bonds). Moreover, the energy difference between **35** and the separate components **34** + AlCl₃ was calculated to be 0.3 kcal mol⁻¹ only. This demonstrates that the dissociation energy needed for this interaction is very small. From a practical standpoint, it means that there is an equilibrium between complex **35** and the two

components **34** + AlCl_3 and it will be shifted toward complex **35** by an excess of AlCl_3 . The existence of this equilibrium thus rationalises the huge amount of aluminium trichloride used in the electrophilic aromatic substitution presented earlier. It is also noteworthy that the fully ionised system $\text{P}^+ + \text{AlCl}_4^-$ is 82 kcal mol^{-1} higher in energy than the loose complex **35** so the possibility of full ionisation of the P-Cl bond is excluded. This finding is in contrast with the work of Niecke described in the introduction of this chapter. The reaction intermediate for the AlCl_3 -induced rearrangement (Scheme 3.1) has been proposed to be the phosphiranylium cation, indicating that the full ionisation of P-Cl took place instead.

Figure 3.3 Computed structure of AlCl_3 -phosphirane loose complex **35**. Selected distances (Å) and angles (deg.): P-W 2.469, P-Cl 2.216, P-C 1.831, Cl...Al 2.479, Al-Cl 2.107 – 2.120 – 2.123; C-P-C 49.21, Cl-P-C 103.79, W-P-C 133.96, W-P-Cl 115.71; P-Cl-Al 121.88; Cl-Al-Cl 115.07 – 118.24 – 117.68.

The Lewis acid-catalysed electrophilic aromatic substitution is reproducible with ferrocene (Scheme 3.9) although it does not proceed with toluene, furan and anisole. It is

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presumed that toluene is not electron rich enough to undergo this electrophilic aromatic substitution. Compared to benzene, heterocyclic aromatic compounds have been noticed to react better with electrophiles because they have much higher electron density than benzene. In the case of furan and anisole, it is postulated that the substitution reaction did not occur due to the strong complexation of AlCl_3 with the oxygen atom (AlCl_3 is highly oxophilic). A theoretical investigation has calculated the donor-acceptor complexation energies of Cl_3Al -furan and Cl_3Al -thiophene to be -14.77 and -8.52 kcal mol $^{-1}$ respectively at B3LYP/6-311G(d,p) + BSSE level,¹⁹ suggesting that the donor-acceptor interaction is stronger in the former complex, which, in turn, reduces the reactivity of AlCl_3 present in the reaction mixture.

Scheme 3.9 AlCl_3 -catalysed electrophilic aromatic substitution of ferrocene

1-ferrocenylphosphirane complex **36** (δ ^{31}P -166.6) is expected to have the same molecular geometry as 1-(2-thienyl)phosphirane complex **33**. In addition, phosphirane complexes **33** and **36** can potentially be precursors of phosphinidene complexes, like 1-chlorophosphirane complex **31**. It will be fascinating to have a precursor of ferrocenylphosphinidene complex **37** since it cannot be synthesised through the established 7-phosphanorbornadiene route. Attempts to prepare 7-ferrocenyl-7-phosphanorbornadiene complex from the [4+2] cycloaddition between the corresponding phosphole complex and dimethyl acetylenedicarboxylate did not succeed as the steric bulk of ferrocenyl group hindered the cycloaddition.²⁰

Ferrocenylphosphinidene **37** was successfully generated from the corresponding phosphirane **31** and trapped by *trans*-stilbene, diphenylacetylene and water to produce

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phosphirane **38** ($\delta^{31}\text{P}$ -130.9), phosphirene **39** ($\delta^{31}\text{P}$ -161.5) and phosphine **40** ($\delta^{31}\text{P}$ 71.0) respectively (Scheme 3.10).

Scheme 3.10 Reaction of ferrocenylphosphinidene complex **37** with several trapping reagents

Figure 3.4 X-ray crystal structure of phosphirane **38**. Selected distances (Å) and angles (deg.):

P1-W1 2.5012(9), P1-C6 1.849(3), P1-C7 1.835(3), P1-C20 1.797(3), C6-C7 1.523(5), Fe1-C20-24 2.038-2.046(4), Fe1-C25-29 2.030-2.044(4); C6-P1-C7 48.84(15), C6-P1-W1 125.80(11), C7-P1-W1 121.34(11), C6-P1-C20 105.87(15), C7-P1-C20 109.64(15), C20-P1-W1 123.07(11).

Ferrocenylphosphirane **31** is now demonstrated to be an efficient precursor of phosphinidene **37** with the fragmentation temperature between 80 and 100°C and cyclohexene as easily-eliminated by-product. The molecular geometry of phosphirane **38** is established by single crystal X-ray structure analysis (Fig. 3.4) whereas phosphirene **39** has been synthesised using a different approach by Sterenberg.¹³

Meanwhile, DFT computation was also performed on the ferrocenylphosphinidene complex **37** at the B3LYP/6-31G(d)-LanI2dz(W) level to investigate its molecular structure.¹⁸ The computed structure (Fig. 3.5) depicts an attractive interaction between the phosphorus and iron atoms. A displacement of phosphorus from the cyclopentadienyl plane toward the iron atom (out of plane angle = 17.6°) can be seen from the structure, which indicates that the electron-rich ferrocenyl substituent clearly affects the electron-deficient phosphorus center. The HOMO-LUMO gap is calculated to be 2.51 eV, larger than that of methylphosphinidene tungsten complex (2.34 eV). From this standpoint, ferrocenylphosphinidene complex **37** can be inferred to be less electrophilic than the *C*-substituted phosphinidene complexes but it still has higher electrophilicity compared to *N*-substituted phosphinidene complexes.

Figure 3.5 Computed structure of ferrocenylphosphinidene complex **37**. Selected distances (Å) and angles (deg.): P21-C16 1.781, P21-W22 2.481. P21-Fe11 3.198; C16-P21-W22 115.51.

3.3 Conclusion

The reactivity of 1-chlorophosphiranes with various nucleophiles has been previously investigated and it has been shown that 1-chlorophosphiranes can provide a convenient access to a variety of phosphiranes by substitution reactions with nucleophiles. However, so far, there is only one investigation on the interaction between 1-chlorophosphirane and Lewis acid and the result is inconclusive.

This chapter explores the chemistry of aluminium trichloride with 1-chlorophosphirane which is annulated to cyclohexane **31**. Ring opening of chlorophosphirane complex **31** to give dichloro(cyclohexyl)phosphine complex **32** was observed from the reaction with AlCl_3 contaminated by HCl. In the presence of thiophene and ferrocene, 1-(2-thienyl)phosphirane complex **33** and 1-ferrocenylphosphirane complex **36** were obtained from chlorophosphirane complex **31** by AlCl_3 -catalysed electrophilic aromatic substitutions. DFT calculations revealed that aluminium trichloride activates chlorophosphirane **31** by weakly coordinating to the chlorine atom of phosphirane **31** to give a loose phosphirane- AlCl_3 complex **35**. However, since the loose complex **35** can dissociate easily, huge quantities of AlCl_3 are needed to push the substitution reaction forward. Meanwhile, no substitution reaction was observed with the less electron-rich toluene. The reaction did not proceed with furan and anisole as well. It is postulated that the strong complexation of AlCl_3 with oxygen atom reduces the reactivity of AlCl_3 and thus, hinders the substitution reaction.

Additionally, 1-ferrocenylphosphirane complex **36** can be utilised as a precursor of ferrocenylphosphinidene complex **37**, thus creating a powerful synthetic tool for ferrocenylphosphines which have numerous applications in homogeneous catalysis. From another standpoint, the successful synthesis of ferrocenylphosphinidene **37** from chlorophosphirane **31** demonstrates the possibility of generating a wide range of other phosphinidene complexes that

cannot be prepared by the classical 7-phosphanorbornadiene route, for example, phosphinidene with very bulky *tert*-butyl substituent as well as silyl- and stannyl-derivatives of phosphinidenes.

3.4 Experimental

All reactions were carried out under nitrogen with distilled dry solvents. All commercially available reagents were used as received from the suppliers unless otherwise specified. Silica gel (230-400 mesh) was used for the chromatographic separations. Cold column chromatography is performed on a jacketed column where low temperature is maintained by a constant flow of chilled solution mixture of water and ethylene glycol. NMR spectra were recorded on either a Bruker BBFO 400 MHz or , AV 400 MHz, or AV 500 MHz spectrometer. All spectra were recorded at 298K. Proton decoupling was applied for ^{13}C and ^{31}P spectra. HRMS were obtained on a Water Q-ToF Premier MS. X-ray crystallographic analyses were performed on a Bruker X8 APEX CCD diffractometer or a Bruker Kappa CCD diffractometer.

(dichloro(cyclohexyl)phosphine)pentacarbonyltungsten (**32**)

Chlorophosphirane **31** (33 mg, 0.07 mmol) was stirred with aluminum trichloride contaminated by HCl (28 mg, 0.21 mmol) in CH_2Cl_2 (2 mL) for 45 min at room temperature. Adding a drop of wet toluene into the mixture favored the reaction. The crude product was purified by chromatography on a jacketed column at -10°C in order to prevent the partial hydrolysis of **32** during the process and eluted with hexane, affording 12 mg of complex **32** (33.7% yield); ^{31}P NMR (CDCl_3) δ 162.9 ($^1J_{\text{PW}} = 320.8$ Hz); ^1H NMR (CDCl_3) δ 1.28 (m, 1H, CH_2), 1.42 (m, 4H, CH_2), 1.79 (d, 1H, $^3J_{\text{HP}} = 12$ Hz, CH_2), 2.02 (s, 2H, CH_2), 2.30 (m, 2H, CH_2), 2.42 (m, 1H, CHP); ^{13}C NMR (CDCl_3) δ 25.75 (s, CH_2), 26.18 (d, $^2J_{\text{CP}} = 15$ Hz, CH_2), 26.97 (d, $^3J_{\text{CP}} = 2.5$ Hz, CH_2), 57.19 (d, $^1J_{\text{CP}} = 5$

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Hz, CHP), 195.08 (d, $^2J_{CP} = 7.5$ Hz, *cis*-CO), 198.01 (d, $^2J_{CP} = 42.8$ Hz, *trans*-CO); MS (*m/z*, relative intensity) 507.9223 (calcd for $C_{11}H_{11}O_5Cl_2PW$ 507.9230).

(7-(2-thienyl)-7-phosphabicyclo[4.1.0]heptane)pentacarbonyltungsten (33)

A mixture of chlorophosphirane **31** (90 mg, 0.19 mmol), aluminum trichloride (151 mg, 1.14 mmol) and thiophene (0.09 mL, 1.14 mmol) was stirred in CH_2Cl_2 (3 mL) for one hour at room temperature. Purification by cold column chromatography ($-10^\circ C$) with hexane as the eluent yielded phosphirane **33** (26 mg, 26.3% yield); ^{31}P NMR (CD_2Cl_2) δ -171.5 ($^1J_{PW} = 269$ Hz); 1H NMR (CD_2Cl_2) δ 1.47 (m, 4H, CH_2), 1.90 (m, 2H, CH_2), 2.28 (m, 2H, CHP), 2.31 (m, 2H, CH_2), 7.08 (m, 1H, C_4H_3S), 7.30 (m, 1H, C_4H_3S), 7.48 (m, 1H, C_4H_3S); ^{13}C NMR (CD_2Cl_2) δ 21.06 (d, $J_{CP} = 4$ Hz, CH_2), 22.06 (d, $J_{CP} = 3$ Hz, CH_2), 26.05 (d, $^1J_{CP} = 14$ Hz, CHP), 127.70 (d, $J_{CP} = 11$ Hz, C_4H_3S), 129.76 (d, $J_{CP} = 2$ Hz, C_4H_3S), 133.98 (d, $J_{CP} = 2$ Hz, C_4H_3S), 139.20 (d, $^1J_{CP} = 24$ Hz, C_4H_3S), 195.66 (d, $^2J_{CP} = 8$ Hz, *cis*-CO), 197.18 (d, $^2J_{CP} = 31.2$ Hz, *trans*-CO); HRMS: *m/z* 519.9709 (calcd for $C_{15}H_{13}O_5PSW$ 519.9731).

(7-ferrocenyl-7-phosphabicyclo[4.1.0]heptane)pentacarbonyltungsten (36)

A mixture of chlorophosphirane **31** (33 mg, 0.07 mmol), aluminum trichloride (55 mg, 0.42 mmol) and ferrocene (78 mg, 0.42 mmol) was stirred in CH_2Cl_2 (2 mL) for one hour at room temperature to give phosphirane **36** which was, then, chromatographed at $-10^\circ C$ with hexane/dichloromethane 9/1 yielding 20 mg (46% yield) of **36**; ^{31}P NMR ($CDCl_3$) δ -166.6 ($^1J_{PW} =$

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264 Hz); ^1H NMR (CDCl_3) δ 1.48 (m, 4H, CH_2), 1.86 (m, 2H, CH_2), 2.05 (m, 2H, CHP), 2.26 (m, 2H, CH_2), 4.18 (d, $J_{\text{HH}} = 2$ Hz, 2H, $\text{C}_5\text{H}_4\text{P}$), 4.23 (s, 5H, C_5H_5), 4.33 (s, 2H, $\text{C}_5\text{H}_4\text{P}$); ^{13}C NMR (CDCl_3) δ 21.57 (d, $^2J_{\text{CP}} = 3.8$ Hz, CH_2), 22.66 (d, $^3J_{\text{CP}} = 2.7$ Hz, CH_2), 26.67 (d, $^1J_{\text{CP}} = 12.3$ Hz, CHP), 69.65 (s, C_5H_5), 70.72 (d, $^3J_{\text{CP}} = 7.5$ Hz, $\text{C}_5\text{H}_4\text{P}$), 71.92 (d, $^2J_{\text{CP}} = 13.4$ Hz, $\text{C}_5\text{H}_4\text{P}$), 79.60 (d, $^1J_{\text{CP}} = 30.4$ Hz, $\text{C}_5\text{H}_4\text{P}$), 196.34 (d, $^2J_{\text{CP}} = 8$ Hz, *cis*-CO), 197.05 (d, $^2J_{\text{CP}} = 29.2$ Hz, *trans*-CO); HRMS: m/z 621.9814 (calcd for $\text{C}_{21}\text{H}_{19}\text{O}_5\text{PWFe}$ 621.9829).

(1-ferrocenyl-2,3-diphenylphosphirane)pentacarbonyltungsten (38)

Ferrocenylphosphirane **36** (40 mg, 0.06 mmol) was stirred with *trans*-stilbene (65 mg, 0.36 mmol) in toluene (2 mL) at 100°C for 7.5 h. Purification by cold column chromatography (-10°C) with hexane/dichloromethane 8/2 gave 15 mg of phosphirane **38** (34.9% yield); ^{31}P NMR (CD_2Cl_2) δ -130.9 ($^1J_{\text{PW}} = 268.9$ Hz); ^1H NMR (CD_2Cl_2) δ 3.70 (s, 2H, CHP), 3.70 (s, 1H, $\text{C}_{10}\text{H}_9\text{Fe}$), 4.22-4.31 (m, 8H, $\text{C}_{10}\text{H}_9\text{Fe}$), 7.23 - 7.47 (m, 10H, aromatic CH); ^{13}C NMR (CD_2Cl_2) δ 35.40 (d, $^1J_{\text{CP}} = 9.7$ Hz, CHP), 39.81 (d, $^1J_{\text{CP}} = 14.6$ Hz, CHP), 70.29 (s, C_5H_5), 71.52 (s, C_5H_4), 71.85 (s, C_5H_4), 71.95 (s, C_5H_4), 76.38 (s, C_5H_4), 76.61 (s, C_5H_4), 127.66 (s, aromatic CH), 128.0 (s, aromatic CH), 129.19 (s, aromatic CH), 129.26 (s, aromatic CH), 129.32 (s, aromatic CH), 129.62 (s, aromatic CH), 130.49 (s, aromatic CH), 135.91 (s, *ipso*-C), 137.56 (s, *ipso*-C), 196.36 (d, $^2J_{\text{CP}} = 8.0$ Hz, *cis*-CO), 197.81 (d, $^2J_{\text{CP}} = 32.3$ Hz, *trans*-CO). HRMS: m/z 720.0004 (calcd. for $\text{C}_{29}\text{H}_{21}\text{O}_5\text{PWFe}$ 719.9986).

(1-ferrocenyl-2,3-diphenylphosphirene)pentacarbonyltungsten (39)

Ferrocenylphosphirane **36** (17 mg, 0.03 mmol) was stirred with diphenylacetylene (32 mg, 0.18 mmol) in toluene (1.5 mL) at 100°C for 7.5 h yielding phosphirene **39** which was then chromatographed at -10°C with hexane/dichloromethane 8/2 as eluent (10 mg, 46.7% yield); ^{31}P NMR (CD_2Cl_2) δ -161.5 ($^1J_{\text{PW}} = 272.2$ Hz); ^1H NMR (CD_2Cl_2) δ 4.16 (s, 5H, C_5H_5), 4.21 (m, 2H, $\text{C}_5\text{H}_4\text{P}$), 4.36 (m, 2H, $\text{C}_5\text{H}_4\text{P}$), 7.50 - 7.93 (m, 10H, aromatic CH); ^{13}C NMR (CD_2Cl_2) δ 70.13 (s, C_5H_5), 71.83 (d, $J_{\text{CP}} = 7.3$ Hz, $\text{C}_5\text{H}_4\text{P}$), 72.74 (d, $J_{\text{CP}} = 14.8$ Hz, $\text{C}_5\text{H}_4\text{P}$), 80.85 (d, $J_{\text{CP}} = 7.8$ Hz, $\text{C}_5\text{H}_4\text{P}$), 128.30 (d, $^2J_{\text{CP}} = 6.2$ Hz, *ipso*-Ph), 129.32 (d, $^1J_{\text{CP}} = 7.8$ Hz, CP), 129.81 (s, aromatic CH), 130.56 (d, $J_{\text{CP}} = 4.8$ Hz, aromatic CH), 130.98 (s, aromatic CH), 196.97 (d, $J_{\text{CP}} = 8.6$ Hz, *cis*-CO), 198.64 (d, $J_{\text{CP}} = 32.6$ Hz, *trans*-CO). HRMS: m/z 717.9829 (calcd. for $\text{C}_{29}\text{H}_{19}\text{O}_5\text{PWFe}$ 717.9858).

(ferrocenyl(hydroxy)phosphine)pentacarbonyltungsten (40)

Ferrocenylphosphirane **36** (12 mg, 0.019 mmol) was stirred with a drop of deionized water in toluene (1.5 mL) at 100°C for 7.5 h. The product was eluted by ethyl acetate from cold column chromatography (-10°C) to give 4 mg (37.7% yield) of **40**; ^{31}P NMR (CH_2Cl_2) δ 71.0 ($^1J_{\text{PW}} = 268.7$ Hz, $^1J_{\text{PH}} = 364.9$ Hz); ^1H NMR (CDCl_3) δ 4.30 (s, 5H, C_5H_5), 4.50 (m, 2H, $\text{C}_5\text{H}_4\text{P}$), 4.55 (s, 1H, $\text{C}_5\text{H}_4\text{P}$), 4.58 (s, 1H, $\text{C}_5\text{H}_4\text{P}$), 8.01 (d, $^1J_{\text{HP}} = 365.2$ Hz, 1H, HP); ^{13}C NMR (CDCl_3) δ 69.60 (s, C_5H_5), 72.11 (d, $J_{\text{CP}} = 9.4$ Hz, $\text{C}_5\text{H}_4\text{P}$), 72.57 (d, $J_{\text{CP}} = 8.6$ Hz, $\text{C}_5\text{H}_4\text{P}$), 72.89 (d, $J_{\text{CP}} = 6.9$ Hz, $\text{C}_5\text{H}_4\text{P}$), 73.33 (d, $^2J_{\text{CP}} =$

20.1 Hz, C_5H_4P), 78.85 (d, $^1J_{CP} = 50.2$ Hz, C_5H_4P), 196.14 (d, $^2J_{CP} = 7.9$ Hz, *cis*-CO), 198.84 (d, $^2J_{CP} = 23.7$ Hz, *trans*-CO); HRMS: m/z (calcd for $C_{15}H_{11}O_6PWFe$ 557.9152). HRMS: m/z 557.9137 (calcd. for $C_{15}H_{11}O_6PWFe$ 557.9152).

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Table A1. Crystal data and structure refinement for compound **6a**.

Identification code	mat171s	
Empirical formula	$\text{C}_{16}\text{H}_{10}\text{O}_{10}\text{P}_2\text{W}_2$	
Formula weight	791.88	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 13.0230(7) Å	a = 90°
	b = 12.1263(7) Å	b = 90°
	c = 13.4177(9) Å	g = 90°
Volume	2118.9(2) Å ³	
Z	4	
Density (calculated)	2.482 g/cm ³	
Absorption coefficient	11.050 mm ⁻¹	
F(000)	1456	
Crystal size	0.060 x 0.080 x 0.080 mm ³	
Theta range for data collection	2.75 to 31.03°	
Index ranges	-18 ≤ h ≤ 18, -17 ≤ k ≤ 17, -19 ≤ l ≤ 19	
Reflections collected	28798	
Independent reflections	3379 [R(int) = 0.0710]	
Completeness to theta = 30.00°	99.9 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.5570 and 0.4720	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3379 / 0 / 136	
Goodness-of-fit on F ²	1.024	
Final R indices [I > 2sigma(I)]	R1 = 0.0272, wR2 = 0.0483	
R indices (all data)	R1 = 0.0538, wR2 = 0.0569	
Largest diff. peak and hole	1.970 and -1.232 e.Å ⁻³	

Table A2. Crystal data and structure refinement for compound **6b**.

Identification code	mat156r	
Empirical formula	C ₁₆ H ₁₀ O ₁₀ P ₂ W ₂	
Formula weight	791.88	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 14.763(4) Å	a = 90°
	b = 9.580(3) Å	b = 92.269(5)°
	c = 15.310(5) Å	g = 90°
Volume	2163.6(10) Å ³	
Z	4	
Density (calculated)	2.431 Mg/m ³	
Absorption coefficient	10.822 mm ⁻¹	
F(000)	1456	
Crystal size	0.24 x 0.30 x 0.34 mm ³	
Theta range for data collection	2.51 to 27.00°	
Reflections collected	4788	
Coverage of Independent reflections	99.2%	
Absorption correction	multi-scans	
Max. and min. transmission	0.1800 and 0.0700	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4795 / 120 / 272	
Goodness-of-fit on F ²	1.115	
Final R indices [I>2sigma(I)]	R1 = 0.0491, wR2 = 0.1215	
R indices (all data)	R1 = 0.0577, wR2 = 0.1288	
Largest diff. peak and hole	2.372 and -2.843 e.Å ⁻³	

Table A3. Crystal data and structure refinement for compound **8**.

Identification code	mat158	
Empirical formula	C ₁₆ H ₁₀ O ₁₀ P ₂ W ₂	
Formula weight	791.88	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 11.0927(6) Å	a = 90°.
	b = 15.1616(9) Å	b = 99.388(2)°.
	c = 12.9297(8) Å	g = 90°.
Volume	2145.4(2) Å ³	
Z	4	
Density (calculated)	2.452 Mg/m ³	
Absorption coefficient	10.913 mm ⁻¹	
F(000)	1456	
Crystal size	0.38 x 0.28 x 0.26 mm ³	
Theta range for data collection	2.09 to 33.48°.	
Index ranges	-15<=h<=16, -21<=k<=22, -19<=l<=18	
Reflections collected	39252	
Independent reflections	6963 [R(int) = 0.0770]	
Completeness to theta = 27.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.1636 and 0.1036	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6963 / 287 / 320	
Goodness-of-fit on F ²	1.149	
Final R indices [I>2sigma(I)]	R1 = 0.0376, wR2 = 0.0953	
R indices (all data)	R1 = 0.0446, wR2 = 0.1005	
Largest diff. peak and hole	1.436 and -6.148 e.Å ⁻³	

Table A4. Crystal data and structure refinement for compound **12**.

Identification code	mat131	
Empirical formula	C ₁₃ H ₁₃ O ₅ PW	
Formula weight	464.05	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.5754(4) Å b = 8.8183(5) Å c = 13.3673(8) Å	a = 72.254(2)°. b = 85.6020(10)°. g = 79.434(2)°.
Volume	725.51(7) Å ³	
Z	2	
Density (calculated)	2.124 Mg/m ³	
Absorption coefficient	8.085 mm ⁻¹	
F(000)	440	
Crystal size	0.30 x 0.26 x 0.20 mm ³	
Theta range for data collection	3.15 to 31.10°.	
Index ranges	-9 ≤ h ≤ 7, -12 ≤ k ≤ 11, -19 ≤ l ≤ 19	
Reflections collected	10463	
Independent reflections	4482 [R(int) = 0.0384]	
Completeness to theta = 30.00°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.2947 and 0.1953	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4482 / 0 / 182	
Goodness-of-fit on F ²	1.062	
Final R indices [I > 2σ(I)]	R1 = 0.0261, wR2 = 0.0548	
R indices (all data)	R1 = 0.0284, wR2 = 0.0555	
Largest diff. peak and hole	2.294 and -2.062 e.Å ⁻³	

Table A5. Crystal data and structure refinement for compound **13**.

Identification code	mat140	
Empirical formula	C ₁₃ H ₁₃ O ₅ PW	
Formula weight	464.05	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pna2(1)	
Unit cell dimensions	a = 23.0597(9) Å	a = 90°.
	b = 10.3519(5) Å	b = 90°.
	c = 6.3109(3) Å	g = 90°.
Volume	1506.49(12) Å ³	
Z	4	
Density (calculated)	2.046 Mg/m ³	
Absorption coefficient	7.788 mm ⁻¹	
F(000)	880	
Crystal size	0.40 x 0.30 x 0.24 mm ³	
Theta range for data collection	1.77 to 43.80°.	
Index ranges	-44<=h<=44, -19<=k<=19, -8<=l<=12	
Reflections collected	26715	
Independent reflections	8062 [R(int) = 0.0534]	
Completeness to theta = 43.80°	98.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.2565 and 0.1467	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8062 / 358 / 246	
Goodness-of-fit on F ²	1.100	
Final R indices [I>2sigma(I)]	R1 = 0.0408, wR2 = 0.0841	
R indices (all data)	R1 = 0.0607, wR2 = 0.1017	
Absolute structure parameter	0.048(12)	
Largest diff. peak and hole	4.142 and -4.646 e.Å ⁻³	

Table A6. Crystal data and structure refinement for compound **33**.

Identification code	mat184	
Empirical formula	C ₁₅ H ₁₃ O ₅ PSW	
Formula weight	520.13	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 8.3993(4) Å	a = 90°
	b = 20.5895(8) Å	b = 107.6813(12)°
	c = 10.2318(4) Å	g = 90°
Volume	1685.87(12) Å ³	
Z	4	
Density (calculated)	2.030 Mg/m ³	
Absorption coefficient	7.792 mm ⁻¹	
F(000)	440	
Crystal size	0.40 x 0.14 x 0.04 mm ³	
Theta range for data collection	3.23 to 28.99°.	
Index ranges	-8<=h<=9, -14<=k<=14, -16<=l<=16	
Reflections collected	17156	
Independent reflections	4047 [R(int) = 0.0255]	
Completeness to theta = 30.00°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.1466	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4047 / 0 / 174	
Goodness-of-fit on F ²	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0167, wR2 = 0.0394	
R indices (all data)	R1 = 0.0210, wR2 = 0.0428	
Largest diff. peak and hole	0.939 and -0.941 e.Å ⁻³	

Table A7. Crystal data and structure refinement for compound **38**.

Identification code	mat188	
Empirical formula	C ₂₉ H ₂₁ FeO ₅ PW	
Formula weight	720.13	
Temperature	183(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 12.1427(6) Å	a = 90°
	b = 18.2553(8) Å	b = 90°
	c = 22.9648(11) Å	g = 90°
Volume	5090.6(4) Å ³	
Z	8	
Density (calculated)	1.879 g/cm ³	
Absorption coefficient	5.187 mm ⁻¹	
F(000)	2800	
Crystal size	0.200 x 0.340 x 0.380 mm ³	
Theta range for data collection	2.68 to 31.03°	
Index ranges	-17<=h<=17, -24<=k<=26, -33<=l<=31	
Reflections collected	53907	
Independent reflections	8113 [R(int) = 0.0588]	
Completeness to theta = 30.00°	99.8 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.4230 and 0.2430	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8113 / 0 / 334	
Goodness-of-fit on F ²	1.095	
Final R indices [I>2sigma(I)]	R1 = 0.0347, wR2 = 0.0632	
R indices (all data)	R1 = 0.0550, wR2 = 0.0690	
Largest diff. peak and hole	1.198 and -0.946 e.Å ⁻³	