Advancing the chemistry of low-valent phosphorus

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2018

Wong, J. Z.-Z. (2018). Advancing the chemistry of low-valent phosphorus. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/81266>

<https://doi.org/10.32657/10220/47470>

Advancing The Chemistry Of Low-Valent Phosphorus

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A thesis submitted to Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy in Chemistry

2018

Acknowledgements

Firstly, I would like to express my upmost gratitude to Professor François Mathey for his guidance and constant encouragement over the course of my stay under his supervision. I am extremely grateful for all that he has done for me, on both a scientific and personal level. He has impacted me in many ways and I will take much of what I have gained with me through my life.

Secondly, I would like to thank Professor Leung Pak-Hing for taking me into his group. He has always been extremely willing to share his deep knowledge and always been most helpful in circumventing any obstacles encountered.

Next, I have to show my appreciation to Dr. Sumod. He accepted me at the end of my freshman year and allowed me to partake in a research program. Without his help over all these years, I would not have achieved what I have.

My mentors, Drs. Xu Chang, Jeanette and Chen Ke have taught me much and I am deeply indebted to them. Dr. Jeremy, with whom I started this research journey, has been a constant companion, learning together along the way. I will never forget most of the “milestones” we have had in the lab.

I have been blessed with the opportunity to mentor a bunch of talented individuals, Sin Yi, Xing Juan, Melody, Sophie, Wei Shi, Odelia and Wang Chang, all of who have taught me something and assisted me along the way. Special thanks must go to Melody, without whom, this dissertation would have been almost impossible to complete in its current form.

I would like to thank lab seniors and friends from both Leung lab and Mathey lab. To Drs. Kennard, Xiang Yuan, Kim, Feny, Yong Xiang and

Vinod, as well as Esther, Cicilia, Duy, Sadeer, Wee Shan, Jia Sheng, Ce Qing, Jeffery, Ronald, Laszlo, David, Xirui, Meldon, Yuet Wan and Shi Min, thank you for all your assistance and for the joy brought to my life. Our yearly outings will be lodged in my memory for a long time to come.

Gratitude must be extended to the Division for a research scholarship, all admin staff, with special thanks to Celine, Ai Hua, Janice, Yean Chin, Susan and Clemence. Drs. Li Yongxin and Rakesh for their expertise in X-ray crystallography, Joan, Wen Wei for their help with elemental analysis and mass spectrometry, and Ee Ling for her assistance in all NMR matters.

Friends must also be included in this soliloquy. To AC Group Zero (Eggy, Reuben, Kangdi and Ashley), Block 38 Sophomores (Yun Long, Lily, Wilfred, Debbie, Chui, Mei Kee, Amanda, Grace, Guan Kang and Kuan Hua), MJ friends (Mr. Lau, De Sheng, Liju, Pangyu, Samuel, Zhitang, Samantha, Fengling, Leon and Yingqi), Sirius seniors, Ariel juniors, and many individuals whom I am unable to list for the sake of brevity, thank you for your friendship and for much laughter brought into my life. It is thanks to you lot that this journey was made with minimal misery.

To my parents for supporting me in all that I do and putting up with my long hours and tired body. I am extremely grateful for all you've done, though I don't say it much and express it poorly.

Last but not least, my fiancée, Chee Shan, for her tolerance and love over the course of my research life, for being a pillar of support and for making me a better person.

Abstract

The chemistry of terminal phosphinidene complexes is deep and rich. Despite the synthetic utility of these highly reactive species, their chemistry is still underdeveloped when compared to both organophosphorus compounds and other low-valent species such as carbenes and nitrenes. In this dissertation, we highlight our efforts at advancing the chemistry of low-valent phosphorus by the grafting of new substituents on to phosphorus and by uncovering new activation modes towards these elusive species.

Summary

This dissertation represents work performed with an aim to further advance the chemistry of low-valent phosphorus, by uncovering new activation modes, new precursors or by grafting new substituents on to the phosphorus atom. Chapter one is an introduction into the area of phosphinidenes (and their complexes). Both their generation modes and key reactions are discussed. Chapter two details the generation of a superelectrophilic phosphinidene complex. The trifluoromethylphosphinidene tungsten(o) complex is trapped with alkynes and electron rich alkenes. The instability of its adduct with *trans*-stilbene highlights the importance of backbonding from phosphorus to olefins in phosphirane complexes. Chapter three concerns the synthesis of 7-phosphanorbornadiene complexes from 7-phosphanorbornene complexes *via* treatment with lithium diisopropylamide, followed by methylation with methyl triflate. These benzoannelated compounds are precursors to terminal phosphinidene complexes. Chapter four highlights an unexpected generation of dianionic phosphides, $[\text{RP} \rightarrow \text{W}(\text{CO})_5]^{2-}$, resulting from an unexpected metalation, leading to a cleavage of the phosphorus bridgehead. These highly reactive species give access to primary phosphine complexes and various phosphorus heterocycle complexes. Lastly, chapter five describes the synthesis of secondary phosphirane complexes as a potential precursor to the parent phosphinidene complex and its unexpected isomerization, generating terminal phosphinidene complexes with no by-products. DFT studies suggest this isomerization takes place through a concerted hydrogen shift.

List of Publications

1. "Isomerization of Secondary Phosphirane into Terminal Phosphinidene Complexes: An Analogy between Monovalent Phosphorus and Transition Metals."

Wong, Jonathan; Li, Yongxin; Hao, Yanwei; Tian, Rongqiang; Mathey, Francois. *Angewandte Chemie International Edition* **2015**, 54 (44), 12891-12893

2. "Generation and Trapping of Terminal Phosphinidene Complex [CF₃P-W(CO)₅]."

Wong, Jonathan; Zhou, Melody; Ganguly, Rakesh.; Mathey, Francois. *ChemistrySelect* **2017**, 2 (30), 9838-9841

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List of Abbreviations and Symbols

δ	NMR chemical shift in Hz
$^{\circ}$	Degree(s)
$^{\circ}\text{C}$	Degrees Celsius
μ	Micro
$\text{\AA}$	Angstrom(s)
Ac	Acetyl
Anal.	Combustion elemental analysis
Ar	Aryl
Bu	Butyl
ca.	<i>circa</i> (Latin: approximately)
calcd.	Calculated
cat.	Catalyst
Cp	Cyclopentadienyl
Cp*	1,2,3,4,5-Pentamethylcyclopentadienyl
Cy	Cyclohexyl
DBU	1,8-Diazabicyclo[5,4,0]undec-7-ene
DCM	Dichloromethane
DEE	Diethyl ether
DFT	Density functional theory

DMAD	Dimethyl acetylenedicarboxylate
E ⁺	Electrophile
EA	Ethyl acetate
Eqv.	Equivalent(s)
ESR	Electron spin resonance
Et	Ethyl
eV	Electronvolt(s)
Fc	Ferrocenyl
Fu	Furanyl
h	Hour(s)
Hex	Hexane
HOMO	Highest occupied molecular orbital
HRMS	High resolution mass spectrometry
iPr	Isopropyl
IUPAC	International Union of Pure and Applied Chemistry
K	Kelvin
kcal	Kilocalorie(s)
LDA	Lithium diisopropylamide
LUMO	Lowest unoccupied molecular orbital
m/z	Mass-to-charge ratio
<i>m</i>	Meta

m	Milli
Me	Methyl
Mes	Mesityl (2,4,6-trimethylphenyl)
Mes*	Supermesityl (2,4,6-tris(<i>tert</i> butyl)phenyl)
mol	Mole(s)
Ms	Methylsulfonyl (mesyl)
NBO	Natural bond order
nBu	n-Butyl
NHC	N-heterocyclic carbene
nm	Nanometer(s)
NMR	Nuclear magnetic resonance
Nu-	Nucleophile
<i>o</i>	Ortho
<i>p</i>	Para
<i>p</i> -tolyl	4-Methylphenyl
Ph	Phenyl
ppm	Parts per million
RT	Room temperature
Sol	Solvent
Stilbene	1,2-Diphenylethylene
t-Bu	<i>Tert</i> butyl

TBAF	Tetrabutylammonium fluoride
TCICA	Trichloroisocyanuric acid
Tf	Trifluoromethanesulfonyl (triflyl)
Th	Thienyl
THF	Tetrahydrofuran
TMS	Trimethylsilyl
TOF	Time of flight
Tol	Toluene
Tolan	Diphenylacetylene
TS	Transition state
UV	Ultraviolet light
ZPE	Zero point energy

1

Introduction

The chemistry of low-valent phosphorus has been largely dominated by phosphorus in the trivalent state. Their most recent advances concern their use in catalysis.¹ Most of these compounds are formed from alkali metal phosphides with appropriate electrophiles or chlorophosphanes with corresponding nucleophiles. A largely neglected route concerns their conversion from monovalent phosphorus compounds. These highly reactive, but elusive species have a fertile chemistry.² The main points, namely their structure and bonding, main modes of generation as well as their key reactions, will be discussed in the following sections.

1.1 Theoretical Description

Phosphinidenes (IUPAC: phosphanylidenes) can be considered to be the phosphorus analogues of carbenes and nitrenes. They are six-electron species that are electron deficient in nature. Although these species have been known for many years, their extreme reactivity has not been exploited to a large extent, a point that will be further elaborated in this section.

Phosphinidenes are compounds with a phosphorus atom which is bonded to one other atom, leaving four electrons in three orbitals. In an extension of a fascinating diagonal relationship between carbon and phosphorus,^{2g, 3} these reactive compounds exist in two forms, the singlet state and the triplet state, just as carbenes do.⁴ The singlet state would distribute the four remaining non-bonding electrons in two pairs (one pair in each orbital), leaving a vacant orbital. The triplet state has two electrons in one orbital, and one

single, unpaired electron with parallel spins in each of the remaining two orbitals.

Figure 1.1 Electronic Structure of Singlet and Triplet Phosphinidenes

The ground state of the parent phosphinidene is the triplet. Theoretical calculations performed at the QCISD(T)/6-311++G(3df,2p) level have estimated the triplet state to be more stable by a formidable 28 kcal mol⁻¹.⁵ Although the presence of π -donating substituents (such as amino, phosphino or alkoxy) on the phosphorus atom can stabilise the singlet state by donation of electron density into the vacant orbital, this additional stabilization alone is insufficient for the singlet state to manifest itself as the ground state. At best, the two states are nearly degenerate. A list of phosphinidenes with their corresponding ground state (triplet) bond lengths and the singlet-triplet gap is found below in Table 1.

Table 1.1 Properties of Free Phosphinidenes⁵

P-R	P-H	P-CH ₃	P-NH ₂	P-OH	P-PH ₂
d _{P-R} / Å	1.415	1.855	1.714	1.665	2.199
$\Delta E_{(S-T)}$ / kcal mol ⁻¹	-28.0	-26.0	-1.2	-16.9	-1.2

Gaspar and co-workers, in 1994, reported that they were able to generate mesitylphosphinidene by irradiating 1-mesitylphosphirane, in the presence

of 3-hexyne, with ultraviolet light at 254 nm at a low temperature of 77 K.⁶ In order to ascertain that a triplet phosphinidene was generated, an electron spin resonance (ESR) spectrum of the glassy matrix was acquired and a high-field signal was observed, which was assigned to the triplet ground state of the free phosphinidene.

However, this result was later found to be erroneous, with the triplet state of oxygen being responsible for the high-field resonance mentioned above. This was confirmed by acquiring an ESR spectrum of the same mixture, but with the introduction of a small air leak at the top of the quartz tube.⁷ Nevertheless, the triplet ground state of free phosphinidenes was confirmed by this subsequent publication, as well as in an independent study by Lammertsma and co-workers.⁸

The triplet ground state of phosphinidenes accords poor control over its reactivity. This, coupled with the harsh conditions needed to generate these compounds, explains the paucity of research in this area.

The non-bonding electrons (lone pair in singlet phosphinidenes, two unpaired electrons in triplet phosphinidenes) have the ability to coordinate to a range of transition metals. In general, when coordinated to a “soft” metal centre with a low oxidation state and π -accepting ligands, the resultant phosphinidene complex is electrophilic in nature. Contrarily, when a phosphinidene is coordinated to a “hard” metal centre with a high oxidation state and σ -donating ligands, the phosphinidene complex is nucleophilic in nature.⁹ Electrophilic phosphinidene complexes are formally composed of the interaction of a singlet phosphinidene with a singlet metal centre. The electrophilicity of the phosphinidene complex is obvious if the bonding

picture is considered. As σ -donation of the phosphorus lone pair is more predominant than π -backbonding from the metal centre, the phosphorus-metal bond is polarized $P^{\delta+}-M^{\delta-}$ and phosphorus has an oxidation state of +1. Formal construction of a nucleophilic phosphinidene complex comprises a triplet metal fragment and a triplet phosphinidene. As phosphorus is more electronegative than the metal centre (in most cases),¹⁰ the phosphorus-metal bond is polarized $P^{\delta-}-M^{\delta+}$ and the phosphorus atom has an oxidation state of +3. While phosphinidene complexes have traditionally been represented as $[R-P=M]$, only the nucleophilic phosphinidene complex has a true double bond; the electrophilic phosphinidene complex is more accurately depicted as $[R-P\rightarrow M]$.¹¹

Figure 1.2 Bonding Framework of Phosphinidene Complexes

Lammertsma and co-workers have conducted a thorough theoretical calculation, approximating the local electron density around the phosphorus atom.¹² They have found that the character of the phosphinidene complex is mainly affected by the ligands around the metal centre. π -accepting ligands such as carbonyl and cyano lower the energy of the π^* orbital, reducing the electron density on the phosphorus atom, making the terminal phosphinidene complex electrophilic. Strong σ -donating ligands such as cyclopentadienyl and halides raise the energy of the π^* orbital, rendering a nucleophilic character to the terminal phosphinidene complex.

The most common complexing groups are the Group VI metal carbonyls. There are several reasons for this. Firstly, the metals (namely chromium, molybdenum and tungsten) are zerovalent. Secondly, the presence of multiple π -withdrawing carbonyl ligands on the metal enhances the electrophilicity of the terminal phosphinidene complex. Lastly, the starting hexacarbonyl complexes are commercially available solids, which are relatively safe to handle, compared to other metal complexes such as tetracarbonyl nickel(0), which is much more toxic.

The added advantage of utilising the Group VI metal carbonyls is that the ground state of these η^1 -terminal phosphinidene complexes is the singlet, offering satisfactory control of its reactivity.⁹ Looking at the pentacarbonyl tungsten(0) series, the singlet phosphinidene complex is more stable than the triplet species across the four terminal phosphinidene complexes surveyed.¹³ Theoretical computations, performed at a high level of theory,¹⁴ have found the energetic difference between the singlet and triplet phosphinidene complex, also known as the singlet-triplet gap (ΔE_{S-T}), to be 9.3 kcal mol⁻¹ for the parent species, $HP \rightarrow W(CO)_5$, increasing to 29.9 kcal mol⁻¹ for the amino-substituted phosphinidene complex, $H_2NP \rightarrow W(CO)_5$.

Table 1.2 Properties of Terminal Phosphinidene Complexes¹³

$(\text{CO})_5\text{W}\leftarrow\text{PR}$	R = H	R = Ph	R = NH ₂	R = OH
$d_{\text{P-R}} / \text{\AA}$	1.458	1.837	1.639	1.699
$d_{\text{M-P}} / \text{\AA}$	2.417	2.423	2.448	2.393
$\Delta E_{(\text{S-T})} / \text{kcal mol}^{-1}$	9.3	10.3	29.9	22.7

Lammertsma and co-workers have also found that for the singlet terminal phosphinidene complexes, the phosphorus-metal bond is shorter (compared to triplet terminal phosphinidene complexes) as a result of π -backbonding from the metal into the vacant p orbital of the phosphorus atom. This bonding picture is further reinforced by the observation that the metal-carbon bond of the *trans*-carbonyl ligand is longer in singlet terminal phosphinidene complexes, a view corroborated by Atwood and co-workers.¹⁵

1.2 Methods Of Generation

This section will detail the methods used to generate phosphinidenes and their complexes. While the emphasis would be placed on the formation of electrophilic terminal phosphinidene complexes, the generation of free phosphinidenes and nucleophilic phosphinidene complexes would be briefly discussed.

1.2.1 Free Phosphinidenes

While free phosphinidenes have been generated by a variety of means, the earliest route to these highly reactive species is from thermal decomposition of cyclopolyphosphanes.¹⁶ These fleeting species were postulated on the basis of products formed from trapping experiments.

Scheme 1.1 Generation of Phosphinidenes From Cyclopolyphosphanes

Later on, mass spectrometry experiments affirmed these suspicions.¹⁷ The signal with $m/e = 108$ was assigned to phenylphosphinidene and correspondingly, the signal with $m/e = 216$ was assigned to its dimer. The evidence for the initial assignment was based on the empirical observation that when the vacuum pyrolyzer was powered down, the signal assigned to phenylphosphinidene vanishes almost instantly, suggesting that this compound is highly reactive and unstable.

Further proof of the existence of free phosphinidenes was uncovered by Schmidt and co-workers.¹⁸ Pentamethylcyclopentaphosphane and pentaethylcyclopentaphosphane were added to the same flask and heated to $150\text{ }^{\circ}\text{C}$. Mass spectrometry analysis of the reaction mixture revealed that all possible combinations of pentaalkylcyclopentaphosphanes were present.

Scheme 1.2 Crossover Experiment Affirming the Generation of Free Phosphinidenes

Another synthetic route to these species is reduction of aryl- or alkylchlorophosphanes with a reactive metal, usually lithium, magnesium or zinc. The formation of these species was inferred from the formation of cyclopolyphosphanes.^{17, 19}

Scheme 1.3 Synthesis of Cyclopolyphosphanes *via* Reduction of Dichlorophosphanes

Retroaddition of phosphiranes can also be used as a method for the generation of free phosphinidenes. One instance of this was reported, by Gaspar and co-workers in their study of 2,4,6-tris(*tert*butyl)phenylphosphinidene.²⁰

Scheme 1.4 [2+1] Retroaddition of Phosphiranes

In 1992, Cowley and co-workers synthesized a bisazide of the formulation $\text{Mes}^*-\text{P}(\text{N}_3)_2$ from reacting $\text{Mes}^*-\text{PCl}_2$ with sodium azide.²¹ Under irradiation with light at a wavelength of 254 nm, a decomposition of the bisazide took place, yielding a secondary phosphine. When done in the presence of a disulfide, insertion into the sulfur-sulfur bond took place, suggesting that a phosphinidene was involved. The bicyclic secondary phosphine formed could be rationalised by phosphinidene formation followed by insertion into a proximal carbon-hydrogen bond.

Scheme 1.5 Cowley's Phosphinidene Generation From Phosphorus Bisazides

Bertrand reported that irradiation of a (phosphino)phosphaketene induced the liberation of carbon monoxide, leaving behind a phosphinophosphinidene.²² There are two noteworthy points of this synthesis. Firstly, this is a rare example of a free phosphinidene having a singlet ground state. This unique property was achieved by having two nitrogen atoms bonded to the phosphino substituent. The congested environment around the diamminophosphino substituent favoured donation of the phosphorus lone pair into the vacant p orbital on the phosphinidene, stabilising the singlet state. Secondly, this singlet phosphinidene was stable enough to be isolated and stored at room temperature. Dimerization was prevented by extensive steric protection, with massive substituents being placed on the β -amino moieties, providing a significant degree of kinetic stabilization.

Scheme 1.6 Bertrand's Free Singlet Phosphinidene

Waterman and co-workers have presented work showing that an iron “half-sandwich” complex was able to catalyse the formation of phosphinidenes from primary phosphines.²³ While not supported fully, a mechanism was postulated, in which the methyl group undergoes a migratory insertion into a carbonyl group, followed by oxidative addition of a phosphorus-hydrogen bond and α -elimination, forming a phosphinidene.

Scheme 1.7 Iron-Catalysed Generation of Phosphinidenes

Another precursor of free phosphinidenes is the polycyclic dibenzo-7-phosphanorbornadiene described by Cummins and co-workers.²⁴ Upon heating with a suitable trapping agent such as cyclohexene or oct-4-yne, a phosphinidene is eliminated, simultaneously forming a molecule of anthracene. These highly strained structures are synthesised from an aminodichlorophosphane and magnesium anthracene dianion.

Scheme 1.8 Generation of Aminophosphinidenes From Dibenzo-7-Phosphanorbornadienes

While this generation mode allows for the formation of phosphinidenes at mild conditions, a severe limitation exists in the variety of substituents that can be grafted onto the phosphorus atom.²⁵ In practise, a π -donor atom needs to be present. Furthermore, bulky substituents such as 2,2,6,6-tetramethylpiperidine are not tolerated. It needs to be highlighted that simple alkyl or aryl substituents such as phenyl also cannot be generated with this precursor, an issue that prohibits widespread use of this modus in synthesis of complex molecular architectures.

A slightly more novel route towards these low-valent species was reported by Stephan and co-workers.²⁶ Starting from a 2*H*-phosphirene, a

rearrangement to a vinylphosphinidene took place upon heating to 110 °C. The novel spiro-bicycle was synthesized from a [2+1] cycloaddition between a cyclic diamidocarbene and a phosphalkyne. It is obvious that this generating method lacks generality, largely in part due to synthetic constraints on both the phosphalkyne and the diamidocarbene. In practise, only two phosphalkynes, namely *tert*butyl- and adamantyl-substituted, have been used with some regularity, probably due to the kinetic stabilization imparted by the extremely bulky groups.

Scheme 1.9 Generation of Phosphinidenes *via* Isomerization From 2*H*-Phosphirenes

1.2.1 Electrophilic Phosphinidenes

Of the types of phosphinidenes (and their complexes) that have been reported in the available literature, the category with the largest synthetic utility is the electrophilic species. It must be pointed out that most examples in this class of compounds are transient, extremely reactive and thus not isolable. Their existence has mostly been inferred from products of trapping reactions, which will be covered in a later section. To date, they have only been detected by mass spectrometry, the most recent of which involves a cationic phosphinidene complex, with the cationic moiety located far from the reactive phosphorus centre, preventing interference with its reactivity.²⁷

This section will highlight the main modes of generation of these highly reactive species and discuss some of their advantages and disadvantages.

1.2.1.1 7-Phosphanorbornadiene

By far, the most versatile and most commonly used precursor for terminal phosphinidene complexes is the 7-phosphanorbornadiene metal complex. The 7-phosphanorbornadiene framework was first synthesized by Mathey and co-workers in 1982.²⁸ Building upon the work in the synthesis of 7-phosphanorbornenes from a phosphole derivative and a reactive alkene such as N-phenylmaleimide,²⁹ the phosphole derivative was reacted with a reactive dienophile, dimethyl acetylenedicarboxylate (DMAD) in this case. The phosphorus atom had to be protected to prevent the phosphole lone pair from attacking the electron deficient carbon-carbon triple bond.³⁰ Oxidation of the phosphole to the phosphole oxide led to dimerization of the resultant compounds even under mild conditions³¹ and while phosphole sulfides are stable at room temperature and pressure, the corresponding 7-phosphanorbornadiene sulfides lose the phosphorus bridge at ambient temperatures, forming a phosphinidene sulfide and an aromatic phthalate.³² The appropriate choice of masking group was found to be the Group VI metal carbonyls.

Scheme 1.10 Synthesis of 7-Phosphanorbornadiene Complexes

The extremely low field chemical shift of 7-phosphanorbornadiene complexes in the ^{31}P NMR spectrum deserves a mention; it is one of the most deshielded observed for a trivalent phosphine complex. However, the most

notable spectroscopic feature was found in the mass spectrometry analysis. These complexes appeared to undergo a cheletropic elimination, eliminating the phosphorus bridge as a terminal phosphinidene complex, $[RP \rightarrow M(CO)_5]$, a hypothesis that was subsequently verified.³³

Scheme 1.11 Terminal Phosphinidene Complex Formation From 7-Phosphanorbornadiene Complexes

7-Phosphanorbornadiene metal complexes have extremely long bridgehead phosphorus-carbon bonds (*ca.* 1.877 Å vs. 1.855 Å³⁴) and a very strained structure (C-P-C intracyclic angle of 79°). The phenyl-substituted 7-phosphanorbornadiene tungsten(o) complex decomposes at above 110 °C, yielding the phenylphosphinidene complex and an aromatic by-product. The attainment of aromaticity in the by-product is the driving force for the reaction to proceed.

The versatility of this route is due to the multitude of R -groups that can be grafted onto the phosphole skeleton, and thereby onto the phosphinidene complex. All of these substrates are synthesized from 3,4-dimethyl-1-phenyl-1*H*-phosphole. The exocyclic cleavage of the phosphorus-phenyl bond by lithium in THF gives the phospholide anion.³⁵ After removal of the phenyl anion with *tert*butyl chloride and coordination to a Group VI metal carbonyl, attack of the resultant tungsten phospholide on an electrophile would give the required phosphole complex. If the substituent is more easily utilised as a nucleophile (such as alkoxy or hydroxy), the phospholide is converted to

the 1-chlorophosphole complex (utilising hexachloroethane)³⁶ or 1-cyanophosphole complex (utilising cyanogen bromide),³⁷ followed by attack of the required nucleophile.

Scheme 1.12 Electrophilic or Nucleophilic Modification of Phosphole Substituent

Despite the apparent versatility of this route, it is not without its limitations. In practise, this method is restricted to diene scaffolds with the two methyl groups. It is fortunate that the two methyl groups make the synthesis of the starting phosphole more convenient and higher yielding than the unsubstituted counterpart.³⁸

The second drawback is that some substituents on phosphorus are not tolerated. One example would be the inability to synthesize the 7-*tert*butyl-7-phosphanorbornadiene tungsten(o) complex. The substituent is too sterically encumbered for the [4+2] reaction to take place, suggesting that the [4+2] cycloaddition is extremely sensitive to the spatial environment of the reactants. This is further validated by the observation that the cycloaddition tends to take place on the opposite side of the metal carbonyl moiety. In addition, nucleophilic groups such as amino and phosphino groups are not tolerated, and attack the carbon-carbon triple bond of the dienophile.

Kinetic studies have been undertaken for the thermal decomposition of 7-phenyl-7-phosphanorbornadiene pentacarbonyltungsten(o) complex.³⁹ It was found that the decomposition was first-order in concentration of the 7-phosphanorbornadiene complex and zero-order in concentration of the trapping agent. It was also found that the nature of the trapping agent had no influence on the rate of the decomposition. The activation barrier was calculated to be around 33 kcal mol⁻¹, consistent with the reaction temperature of above 110 °C.

The activation energy of the cheletropic elimination can be lowered by the addition of copper(I) chloride.⁴⁰ Both the reaction time and reaction temperature were drastically lowered. While atypical, the addition of copper(I) chloride also can alter the course of the reaction. One striking example would be the generation of a phosphinidene complex from 7-chloromethyl-7-phosphanorbornadiene tungsten(o) complex.⁴¹ When decomposed under thermal conditions at 110 °C, the expected terminal phosphinidene complex is formed. When decomposed at 60 °C in the presence of copper(I) chloride, a rearrangement occurs, forming the methylenechlorophosphane complex.

Scheme 1.13 Alteration of Decomposition Pathway By Addition of Copper(I) Chloride

Theoretical studies have shown that copper(I) ion interacts with the phosphorus atom, the tungsten(o) atom and one of the bridging carbons, transferring the chloride to the phosphorus atom, while concomitantly

cleaving both phosphorus-carbon bridges.⁴² The copper(I) ion is stabilised by coordination to a molecule of solvent. Upon attack of the trapping agent on the phosphorus atom, the chloride ion is shuttled back to the copper(I) ion in an “S_N2-like” manner, regenerating the active catalyst. This mechanism implies that when the cheletropic elimination is mediated by copper(I) chloride, a terminal phosphinidene complex is not formed. Instead, the reactive intermediate formed is a phosphinidenoid complex. This computational study, while done at a high level of sophistication, is unable to explain why the copper(I) chloride-catalysed decomposition works only with the tungsten-coordinated 7-phosphanorbornadiene, a point which must be emphasized, though not commonly discussed.

Scheme 1.14 Mechanism of Copper(I) Chloride-Catalysed Decomposition of 7-Phosphanorbornadiene Tungsten(0) Complexes

In the presence of copper(I) chloride, the rate of decomposition of 7-phenyl-7-phosphanorbornadiene pentacarbonyltungsten(o) complex can be accelerated by increasing substrate concentration. Lammertsma and Bickelhaupt have studied this effect in their study of addition of terminal phosphinidene complexes to dienes.⁴³ When the concentration of diene was increased, the rate of cheletropic elimination was increased, but by a factor much smaller than if strict first-order kinetics were obeyed. While no satisfactory explanation can be proposed for this observation, the authors speculate that a complex between the copper(I) ion and the 7-

phosphanorbornadiene complex may be formed at a low steady-state concentration, followed by its decomposition in the rate-determining step. The activation energy of the copper(I) chloride decomposition was found to be around 15 kcal mol⁻¹.

1.2.1.2 Phosphiranes

Phosphirane complexes have also been shown to eliminate terminal phosphinidene complexes. This process occurs *via* a [2+1] retroaddition.

Scheme 1.15 Retroaddition of Phosphirane Tungsten(0) Complexes

The cleavage of the two phosphorus-carbon bonds is symmetry allowed⁴⁴ and occurs synchronously.

This generating method was first reported in 1985 by Mathey and co-workers.³⁹ 1,2,3-Triphenylphosphirane pentacarbonyltungsten(o) was reacted with diphenylacetylene at 150 °C, forming the corresponding phosphirene complex. The harsh conditions reflect the stability of phosphirane complexes, when compared against the previously described 7-phosphanorbornadiene complexes.

Scheme 1.16 First Reported Generation of Terminal Phosphinidene Complexes from Phosphirane Complexes

Miqueu and co-workers have reported that phosphirane complexes are less efficient precursors to terminal phosphinidene complexes than the

corresponding 7-phosphanorbornadiene complexes, akin to what is observed on a practical level.⁴⁵ It was reported that the energy barrier for generation of phenylphosphinidene pentacarbonyltungsten(o) is higher when generated from phosphiranes (27.5 kcal mol⁻¹) than from 7-phosphanorbornadiene (23.5 kcal mol⁻¹). In addition, the [2+1] retroaddition is endergonic and probably reversible, whereas the cheletropic elimination is exergonic and essentially, irreversible.

This method of generation did not find much of an application, possibly due to the high temperature required, until 1989 when Mathey changed the alkyl (or aryl) substituent on phosphorus to an amino group.⁴⁶ In a mode analogous to that of singlet carbenes, the lone pair on the nitrogen atom stabilises the singlet state by interacting with the vacant p orbital on the terminal phosphinidene complex. This stabilization was sizeable, allowing for decomposition of aminophosphirane complexes at temperatures of around 70 °C to 90 °C. This route was essential, providing the first viable route to aminophosphinidene complexes, due to the incompatibility of the phosphorus-nitrogen bond with DMAD as highlighted earlier. Aminophosphirane complexes were formed from the deprotonation of primary aminophosphane complexes with a base, followed by cyclization with dichloroethane.

Scheme 1.17 Generation of Aminophosphinidene Complexes

In 2009, Mathey and co-workers synthesized a chlorophosphirane complex, derived from the [2+1] cycloaddition of cyclohexene and

chlorophosphinidene tungsten(o) complex.³⁶ The stereochemistry of this cycloaddition deserves special mention; the more hindered *cis*-isomer was formed almost exclusively, as compared to the non-separable mixture when the phenyl derivative was synthesized.⁴⁰

Scheme 1.18 One-Pot Generation of Chlorophosphirane Tungsten(0) Complex

Further investigation revealed that this phosphirane complex was an extremely efficient precursor of chlorophosphinidene complex. Heating the chlorophosphirane complex in the presence of diphenylacetylene for 2 hours at 70 °C yielded the expected phosphirene complex. One practical advantage of this method is that the by-product, cyclohexene in this case, is a low boiling point liquid, and could be easily removed under reduced pressure, negating the need for tedious separation by column chromatography. This circumvents an obstacle faced when the 7-phosphanorbornadiene metal complex route is used and a polar phosphine complex is formed, which often co-elutes with the phthalate.

Scheme 1.19 Retroaddition of Phosphirane Tungsten(0) Complex

In 2014, Mathey and co-workers, leveraging on the diastereoselective formation of the aforementioned chlorophosphirane complex, activated the phosphorus-chlorine bond with aluminium chloride in a Friedel-Craft-type

reaction with ferrocene.⁴⁷ The resultant ferrocenylphosphirane complex was decomposed at 100 °C. The formation of ferrocenylphosphinidene tungsten(o) complex would not have been possible with the 7-phosphanorbornadiene route due to the steric congestion hindering the [4+2] cycloaddition with dimethyl acetylenedicarboxylate.

Scheme 1.20 Generation of Ferrocenylphosphinidene Complex

1.2.1.3 Phosphirenes

1*H*-Phosphirenes are the unsaturated analogues of phosphiranes. Phosphiranes are markedly more stable than phosphiranes due to the stabilising interaction of the low-lying, vacant orbital at phosphorus and the *p* orbitals of the carbon-carbon double bond.

The stability of this species is evident in the high reaction temperature required for the generation of terminal phosphinidene complexes. Only the generation of aminophosphinidene (once again, due to the stabilization of the nitrogen lone pair) has been achieved, albeit under extremely harsh conditions of 130 °C for extended periods of time.⁴⁶

Scheme 1.21 Generation of Diethylaminophosphinidene Complexes From Phosphirenes

1.2.1.4 Azaphosphirenes

In 1994, Streubel and co-workers were able to generate terminal phosphinidene complexes from 2*H*-azaphosphirene complexes.⁴⁸ It was

initially believed that the decomposition of these species is analogous to that of phosphirane complexes, in which simultaneous cleavage of the phosphorus-carbon and phosphorus-nitrogen bonds take place. It was later reported that based on a series of control experiments, a two-step mechanism was more plausible.⁴⁹ It begins with a phosphorus-carbon bond cleavage, forming a transient nitrillium-phosphane ylide, followed by phosphorus-nitrogen bond cleavage, eliminating an aryl nitrile and the expected terminal phosphinidene complex. In a subsequent publication, the same research group showed that the nitrillium-phosphane ylide could also be generated in the presence of ultraviolet light at low temperatures, in a much more efficient manner than under thermal conditions.⁵⁰ Upon warming, the terminal phosphinidene complex is formed.

Scheme 1.22 Formation of Nitrillium-Phosphane Ylides From Azaphosphirene Complexes and Subsequent Decomposition Into Terminal Phosphinidene Complexes

There are currently two synthetic routes towards *2H*-azaphosphirene complexes. The first route relies on a condensation-rearrangement route of an aminocarbene pentacarbonyltungsten(o) complex and bis(trimethylsilyl)methylenechlorophosphane. In the presence of triethylamine as a base, a condensation reaction takes place, forming an intermediate, which undergoes a facile 1,3-hydrogen shift, yielding a 1-phospha-4-metallobutadiene. This then undergoes a rearrangement, with a

transfer of the pentacarbonyltungsten(0) complexing group from the carbon to the phosphorus atom.⁵²

Scheme 1.23 Synthesis of Azaphosphirene Complex From Aminocarbene Tungsten(0) Complex and a Phosphaalkene

The second route involves the reaction of an aminocarbene complex with a pentamethylcyclopentadienyl-substituted dichlorophosphane.⁵³ In the presence of triethylamine, a nucleophilic attack of the nitrogen lone pair on the phosphorus-chlorine bond takes place, which then undergoes either a further condensation, or a base-induced elimination, yielding a 1-phospha-4-metallobutadiene, analogous to what is observed above.

Scheme 1.24 Synthesis of Azaphosphirene Complex From Aminocarbene Tungsten(0) Complex and Dichlorophosphane

The major drawback of this mode of generation lies in the limited substrate scope. In practice, the first route is limited to bis(trimethylsilyl)methyl substitution on the phosphorus atom. While the second route appears initially to be fairly general, it seems restricted to the pentamethylcyclopentadienyl, triphenylmethyl or 2,4,6-triisopropylphenyl.⁵⁴ Smaller substituents such as phenyl or methyl, as well as larger substituents such as 2,4,6-tris(*tert*butyl)phenyl, do not yield the desired 2*H*-azaphosphirene complex, instead giving multinuclear carbene complexes with bridging phosphorus atoms. The advantage using 2*H*-azaphosphirene complexes as precursors must be noted, being able to yield bulky terminal phosphinidene complexes which provides kinetic stabilization of products of trapping reactions.

1.2.1.5 3*H*-Benzophosphepines

In 1999, Gajewski and co-workers published a theoretical study on the interconversion of norcaradiene and 1,3,5-cycloheptatriene.⁵⁵ The energy difference between the two forms is estimated to be *ca.* 4 kcal mol⁻¹ (with the cycloheptatriene being more stable) as well as an energy barrier of around 11 kcal mol⁻¹.⁵⁶

Scheme 1.25 Tautomerization of Cycloheptatriene and Norcaradiene

Inspired by this, Lammertsma and co-workers reported in 2005 that for the phosphorus analogues, phosphepines are less stable than the corresponding phosphanorcaradienes.⁵⁷ In another example of how transition metal complexation provides a large degree of stabilization, it was found that when

a pentacarbonyltungsten(o) fragment was complexed on the phosphorus atom, the phosphepine complexes were found to be more stable. This stability was further enhanced by benzoannulation, probably due to conjugation, with a combined energy difference of 16.8 kcal mol⁻¹.

The 3*H*-benzophosphepine complex undergoes an electrocyclization at elevated temperatures of around 80 °C, forming a phosphanorcaradiene complex.⁵⁸ The instability of these strained, tricyclic structures causes its decomposition into a terminal phosphinidene complex as well as an aromatic by-product, naphthalene in this case. It can be assumed that the attainment of aromaticity in the naphthalene ring provides the driving force for this reaction.

Scheme 1.26 Generation of Terminal Phosphinidene Complexes From Benzophosphepine Complexes via a Phosphanorcaradiene Intermediate

3*H*-Benzophosphepine complexes are synthesized from a double hydrophosphination of a primary phosphine complex on 1,2-diethynylbenzene.

Scheme 1.27 Synthesis of 3*H*-Benzophosphepine Complexes

The advantage of this route is that different transition metal complexes (Group VI metal carbonyls & cyclopentadienyldicarbonylmanganese(I)) are tolerated, though best results are still achieved with pentacarbonyltungsten(o) as a complexing group. A significant limitation of this route would be the vastly reduced flexibility in the choice of phosphorus substituent due to the problems with synthesis of the required primary phosphine complex.

1.2.1.6 Salt Metathesis

The next route of generation of terminal phosphinidene complex is salt metathesis, mainly between a dichlorophosphane and Collman's reagent.

The first reported reaction of Collman's reagent with a dichlorophosphane was in 1983 by Power and co-workers.⁵⁹ Here, even though terminal phosphinidene complexes were not mentioned, it is likely that dimerization of these highly reactive species were responsible for the formation of the diphosphene complex.

Scheme 1.28 Formation of Phosphinidene Complex by Salt Metathesis and Subsequent Dimerization

Shortly after, the same group reported that when the tetracarbonyliron(o) was swapped out for pentacarbonylchromium(o), an analogous 1,2-diphosphene was isolated along with two complexes with bridging phosphinidene units.⁶⁰ This observation unequivocally showed that terminal phosphinidene complexes are formed and were probably responsible for the formation of the diphosphene complex.

Scheme 1.29 Reaction of $\text{Na}_2\text{Cr(CO)}_5$ and Dichlorophosphane Giving a Range of Phosphinidene Derivatives

King and co-workers, when investigating the reaction of (dialkylamino)dichlorophosphanes with Collman's reagent, observed the formation of iron carbonyl clusters with bridging phosphane units.⁶¹ A mechanism was proposed for the formation of the cluster formed from (diethylamino)phosphorus dichloride. It was hypothesized that the cluster formed from a series of phosphinidene formation, dimerization and migration of amino moieties.

Intrigued by King's hypothesis, Lammertsma, in 1999, attempted to trap the extremely reactive iron terminal phosphinidene complex with a range of alkenes and alkynes.⁶² The generation at $-30\text{ }^\circ\text{C}$ proceeded smoothly, but trapping of these elusive molecules could not be achieved, with cluster formation being preferable to cycloaddition. Increasing the electron density around the olefinic double bond was not sufficient for induction of cycloaddition. This necessitated a judicious choice of trapping agent for the corresponding phosphirane complex to be formed; 1,2-propandiene and tetramethyldiallene were used to form the corresponding phosphirane complexes, though the phosphirane complexes generated from

tetramethyldiallene isomerized into a phospholene complex at elevated temperatures.

Scheme 1.30 Lammertsma's Generation of Aminophosphinidene Iron(0) Complex and Its Subsequent Trapping

It must be noted at this juncture that “traditional” trapping agents such as stilbene and styrene were unsuccessful in generating the corresponding phosphirane complexes, highlighting the reduced electrophilicity of the dialkylaminophosphinidene tetracarbonyliron(0) when compared against its phenylphosphinidene pentacarbonyltungsten(0) counterpart. Two aspects of this complex give rise to its compromised electrophilicity. Firstly, even though the nitrogen atom is electronegative, it is a good π -donor, donating electrons into the vacant p orbital on phosphorus, increasing the electron density. Secondly, the tetracarbonyl iron(0) fragment, with one less strongly electron withdrawing carbonyl ligand than pentacarbonyltungsten(0), does not draw electron density away from the phosphorus atom as efficiently.¹²

In 2016, Lammertsma found that if the aminophosphinidene complex were formed in olefinic solvent, it was possible to store the phosphirane complex as a “bottled” phosphinidene source.⁶³ Formed in 1-hexene, the corresponding phosphirane complex was able to be transferred to other

trapping agents such as alkynes, primary amines, secondary amines and alcohols.

While this method allows for the formation of phosphinidene complexes at extremely mild conditions (between $-70\text{ }^{\circ}\text{C}$ and $-30\text{ }^{\circ}\text{C}$), there are a few hurdles in the usage of this synthetic protocol. The metal complexing group is limited to tetracarbonyl iron(0) due to the necessitated use of Collman's reagent. In practise, only dialkylamino species have found some synthetic utility. The low generating temperature, coupled with the low electrophilicity renders this approach to be less viable due to the preference of the system to form the aforementioned iron-phosphorus clusters.

1.2.2 Cationic Stable Phosphinidenes

There is a class of electrophilic phosphinidene complexes that are stable. These cationic phosphinidene complexes are usually isolable in their solid states, albeit with a propensity to undergo hydrolysis with adventitious water and must be handled under strictly anhydrous conditions.

These complexes were first synthesized by Carty and co-workers in 2001⁶⁴ with molybdenum, tungsten and ruthenium but other metals have also been utilised.⁶⁵ In general, the synthetic protocol starts with a metal chlorophosphide complex followed by chloride abstraction using a Lewis acid, normally aluminium trichloride. Their structural data are fairly similar with the tungsten analogue showing a phosphorus-metal bond length of $2.4503(6)\text{ \AA}$ and a bond angle of $118.69(8)^{\circ}$ around the phosphorus atom. The short phosphorus-nitrogen bond length of $1.629(2)\text{ \AA}$ is indicative of π donation from nitrogen to the vacant p orbital on phosphorus. This is further corroborated by planarity around the nitrogen atom (sum of bond angles =

360°). They are also characterised by an extremely low field ^{31}P NMR resonance of +939 ppm for the tungsten compound.

Scheme 1.31 Carty's Generation of Cationic Stable Phosphinidenes By Chloride Abstraction

The iron phosphinidene complex deserves special mention. Its synthesis was first attempted in 1984 by Gladysz and Bertrand.⁶⁶ Treatment of an iron anion by aminodichlorophosphane yielded the iron phosphide complex. Abstraction of chloride by aluminium chloride was performed and a ^{31}P NMR resonance with no significant proton coupling was detected at +954 ppm at -90 °C. Upon warming, this signal rapidly disappeared and formed three diastereomers at +184, +152 and +124 ppm with phosphorus-hydrogen coupling constants of between 437 Hz and 459 Hz. These results were rationalised as the formation of a phosphinidene complex, which then inserts into a carbon-hydrogen bond of an isopropyl group, forming a four-membered ring.

However, in 2003, Carty and co-workers managed to isolate the iron phosphinidene complex by ensuring that the environment was rigorously anhydrous.^{65a} A structural analysis revealed a phosphorus-iron bond length of around 2.151 Å and a bond angle of 118.6° around the phosphorus atom.

1.2.3 Nucleophilic Phosphinidenes

In the past three decades, there has been an incredible growth in the synthesis of nucleophilic phosphinidene complexes, despite their drastically diminished applicability in the synthesis of phosphorus-containing molecules, especially when compared to their electrophilic counterparts. This phenomenon can be attributed to their superior stability, allowing for their complete characterization by multinuclear NMR and X-ray crystal structure analysis. Much of their chemistry has been described by Cowley⁶⁷ and recently updated by Lammertsma and co-workers.^{2f} Their pertinent structural features and synthetic routes will be covered in this section.

Broadly speaking, amongst the few routes towards the generation of these nucleophilic phosphinidene complexes, the most widely used method is the formation of a phosphorus-metal bond by salt metathesis, followed by elimination of a small molecule, allowing for the formation of a double bond between the phosphorus and metal atoms.

The first successful synthesis and isolation of these species was by Lappert in 1987.⁶⁸ Starting with a lithium metal hydride and a phosphorus dichloride, initial phosphorus-metal bond was formed with concomitant formation of lithium chloride. Phosphinidene formation was achieved by elimination of hydrogen chloride. The two metal complexes with molybdenum and tungsten had an extremely low field chemical shift ($\delta = +661$ ppm for tungsten with a coupling constant of 153.5 Hz) and a short phosphorus-metal bond (2.349(5) Å).

Scheme 1.32 Phosphinidene Complex Formation From Lithium Metal Hydride and Dichlorophosphane

Indeed, this method also works with reverse polarity, with a metal-chlorine bond and a lithium phosphide. This method was exploited by Stephan and co-workers for the synthesis of a zirconium phosphinidene complex.⁶⁹ Starting from a zirconium dichloride and a lithium phosphide, a diphosphido species is formed. On the basis of products formed, it was hypothesized that a phosphinidene was formed, with a concomitant formation of a primary phosphine. X-ray structure analysis revealed a short phosphorus-zirconium bond length of 2.505(4) Å and a bent geometry around the phosphorus atom (101.4(1)°). Similar to the Lappert's phosphinidene complex, they resonate at extremely low field in the ³¹P NMR spectrum, having a chemical shift of +792.7 ppm.

Scheme 1.33 Phosphinidene Complex Formation From Metal Phosphide and Zirconium Dichloride

In a similar vein, Schrock and co-workers were able to synthesize a tantalum phosphinidene complex by utilization of an extremely bulky tetradentate ligand, providing a huge degree of kinetic stabilization.⁷⁰ The sterically imposing ligand induces linearity of the phosphinidene, which compels a tantalum-phosphorus pseudo-triple bond, as evidenced by a dramatically shortened bond length. This method has the unique advantage of being able

to modify the phosphinidene substituent after successful formation of the phenyl phosphinidene complex.⁷¹ The addition of elemental lithium causes cleavage of the phosphorus-carbon bond, yielding a terminal phosphido complex. Addition of an electrophile would then result in the formation of a phosphinidene with a variety of phosphorus substituents. These compounds have a linear geometry around the phosphorus atom (170.9° for $R = \text{cyclohexyl}$) and a short metal-phosphorus bond ($2.145(7) \text{ \AA}$ for $R = \text{cyclohexyl}$), indicative of a phosphorus-metal triple bond. They resonate at high fields in the ^{31}P NMR spectrum, with signals being found ca. $+200 \text{ ppm}$.

Scheme 1.34 Synthesis of Schrock's Tantalum Phosphinidene Complex

In the early 2000's, it was shown by Lammertsma and co-workers that this route could be utilised for the synthesis of phosphinidene complexes with late transition metals, iridium in this case.⁷² First, pentamethylcyclopentadienyl iridium(III) chloride dimer was treated with triphenylphosphine or an N-heterocyclic carbene (NHC). Subsequent treatment with a lithium phosphide yielded the iridium-bound phosphinidene complex. Both these complexes were characterised by X-ray crystal structure analysis and were found to be similar. With triphenylphosphine as the ancillary ligand, a bond angle of $113.73(7)^\circ$ was observed at the phosphorus atom. The iridium-phosphorus bond length of $2.2121(5) \text{ \AA}$ is typical for a metal-phosphorus double bond. This complex displays a ^{31}P chemical shift of $+686.6 \text{ ppm}$.

Scheme 1.35 Synthesis of Iridium Phosphinidene Complex *via* Salt Metathesis

In the same publication, it was demonstrated that the same phosphinidene complex can be generated by an alternate route.^{72a} Initial coordination of a primary phosphine to iridium, followed by a double dehydrohalogenation yields the 16e⁻ nucleophilic phosphinidene complex. This reactive intermediate is intercepted by a donor ligand, triphenylphosphine in this case, forming the stable iridium phosphinidene complex. This route is fairly general, with a wide range of other ligands such as phosphines, phosphites, arsines, isocyanides and carbon monoxide, proving viable for this mild procedure. In addition, this reaction sequence can be utilised for other members of the Group IX triad and has been extended to the Group VIII metals, albeit with minor modifications to the reaction conditions.⁷³

Scheme 1.36 Synthesis of Iridium Phosphinidene Complex *via* Double Dehydrohalogenation

When conditions permit, the adduct formed from the first step in a salt metathesis can be intercepted and led down a different mechanistic pathway. Niecke and co-workers postulated that migration of the hydrogen onto the phosphorus substituent allowed for the formation of a nucleophilic phosphinidene complex.⁷⁴ This reaction pathway was proposed on the basis

of an observed signal of the tungsten analogue at $\delta = +754$ ppm in the ^{31}P NMR spectrum recorded at -40°C . Upon warming, the signal decreases in intensity, forming the target nucleophilic phosphinidene complex *via* a 1,3-hydrogen migration.

Scheme 1.37 Phosphinidene Complex Formation by α -Hydrogen Migration

Another route that has led to nucleophilic phosphinidenes is the oxidative addition of a phosphorus-hydrogen bond to a metal, followed by elimination of a small molecule. This was the route taken by Wolczanski in their synthesis of a tantalum phosphinidene complex.⁷⁵ Starting from phenylphosphine, tantalum was added across the phosphorus-hydrogen bond, followed by dihydrogen elimination, forming the phosphinidene. The tantalum-phosphorus bond was short at 2.317(4) Å with a bent structure (bond angle of $110.2(4)^\circ$ at phosphorus). A chemical shift of +334.6 ppm was observed.

Scheme 1.38 Phosphinidene Complex Formation by Insertion and Elimination

Cowley and co-workers have used phosphinidene group transfer reagents to create tungsten phosphinidene complexes.⁷⁶ Reacting a phosphaketene with a dichlorotetraphosphane tungsten complex, a formal insertion into the phosphorus-carbon double bond was observed with the liberation of two

units of phosphine, forming a linear phosphinidene complex. The chemical shift of +193 ppm and phosphorus-tungsten coupling constant of 649 Hz is vastly different from what was synthesized by Lappert to exclude the possibility of a bent phosphinidene complex. Its structure was confirmed with an X-ray crystal structure, showing a phosphorus-tungsten bond length of 2.169 Å and a bond angle of 168.2(2)°, providing structural confirmation of a linear phosphinidene with a phosphorus-tungsten triple bond.

Scheme 1.39 Phosphinidene Complex Formation by Group Transfer

The formation of nucleophilic phosphinidenes *via* ring opening of tantalaziridine complexes has been achieved by Cummins and co-workers.⁷⁷ Attack of a secondary phosphide on a tantalum centre in a three-membered ring, followed by migration of a hydrogen atom from phosphorus to the ring carbon yields the tantalum-bound phosphinidene complex. This complex resonates at +451.6 ppm in the ³¹P NMR spectrum. The phosphorus-tungsten bond length was found to be 2.3051(1) Å with a bond angle of 125.15(13)° around phosphorus.

Scheme 1.40 Phosphinidene Complex Formation by Ring Opening Followed by Hydrogen Migration

A final method for synthesis of these compounds is reported by Hillhouse and co-workers.⁷⁸ Starting from a diphosphine nickel chloride dimer, it was converted to the nickel phosphide complex by addition of a secondary lithium phosphide. Oxidation by tropylium, followed by deprotonation yields the nickel phosphinidene complex. The phosphinidene phosphorus resonates as a triplet at an extremely low field of +970 ppm with a coupling constant of 134 Hz. The X-ray crystal structure revealed a phosphorus-nickel bond length of 2.0772(9) Å with a bond angle of 130.8(1)° at the phosphinidene phosphorus.

Scheme 1.41 Phosphinidene Complex Formation by Oxidation and Deprotonation

1.3 Reactions

These compounds are highly reactive with a short lifetime. As such, most of these compounds are generated from an appropriate precursor and trapped *in situ* with a variety of trapping agents. The existence of phosphinidenes has been postulated on the basis of mass spectrometry and from logical deduction from isolation of the trapping products.

1.3.1 Free Phosphinidenes

As mentioned previously, the chemistry of free phosphinidenes lacks the depth of other low-valent species such as carbene, nitrenes or even terminal phosphinidene complexes for that matter. However, there are a few reactions

that are unique to these elusive species and will be covered briefly in this section.

When generated in the absence of a trapping agent, phosphinidenes can insert into a vicinal carbon-hydrogen bond, forming a secondary phosphine. This was first demonstrated by Cowley and co-workers in 1992 when they successfully generated 2,4,6-tris(*tert*butyl)phenylphosphinidene, which inserted into one of the carbon-hydrogen bonds of the *ortho-tert*butyl groups.²¹

Scheme 1.42 Insertion of Phosphinidenes Into Vicinal C-H Bond

Phosphinidenes have been added across the sulfur-sulfur bond of disulfides. In 1968, Schmidt and co-workers reported the successful insertion of phenylphosphinidene (generated from pentaphenylcyclopolyphosphane) into diethyldisulfide in high yields.⁷⁹

Scheme 1.43 Insertion of Phosphinidenes Into S-S Bonds

Phosphorus-phosphorus bonds can also be cleaved by phosphinidenes. Reaction of tetrakis(trifluoromethyl)cyclotetraphosphane (a precursor to transient trifluoromethylphosphinidene) in the presence of tetramethyldiphosphane yielded a triphosphane after 13 days at ambient

temperatures.⁸⁰ In a similar vein, the same phosphinidene inserts into arsenic-arsenic bonds, forming the bisarsinophosphane.⁸¹

Scheme 1.44 Insertion of Trifluoromethylphosphinidene Into P-P and As-As Bonds

Schmidt and co-workers were able to form dibenzophospholes by insertion of phenylphosphinidene into a carbon-carbon bond of biphenylene, albeit with extremely drastic conditions.⁸² The reaction is probably driven by the mild anti-aromaticity and ring strain of the four-membered ring.⁸³ The modest yield of this reaction prevents it from being used as a logical route to dibenzophospholes.

Scheme 1.45 Phosphinidene Insertion Into C-C Bond of Biphenylene

Schmidt also reported the formation of 3-phospholenes and tetrahydro-1,2-diphosphinines by heating pentaphenylcyclopentaphosphane with 1,3-dienes.⁸⁴ The photochemical generation of phenylphosphinidene led to only the formal [4+2] addition product.

Scheme 1.46 Reaction of Phosphinidenes With Dimethylbutadiene

A final example of phosphinidene reactivity is a curious, unique example. Upon thermolysis of vinylphosphirane, an isomerism of vinylphosphinidene takes place, yielding methylphosphaalkyne.⁸⁵ Theoretical investigations into a plausible mechanism have found that vinylphosphinidene, *2H*-phosphirene and phosphallene are in rapid equilibrium. However, the conversion from vinylphosphinidene to methylphosphaalkyne is irreversible from both a kinetic and thermodynamic standpoint, explaining the exclusive formation of the phosphaalkyne.⁸⁶

Scheme 1.47 Isomerization of Vinylphosphinidene Into Methylphosphaalkyne

1.3.2 Electrophilic Phosphinidene Complexes

Electrophilic phosphinidenes complexes have a much wider reaction scope as compared to the uncomplexed variant. As described in a preceding section, this is largely in part due to the singlet state of these species, giving a large degree of control of its reactivity.

1.3.2.1 No Trapping Agent

When generated with copper(I) chloride in the absence of a trapping agent, these reactive species dimerize, forming a diphosphene.⁸⁷ This technique to

form diphosphenes appears to be fairly general.⁸⁸ Methyl, thienyl, pyrrolyl and ester moieties are tolerated, though the methyl variant was too unstable to be isolated and had to be trapped by 2,3-dimethylbutadiene and characterised as its [4+2] cycloadduct. Cyano groups hinder the extrusion of phosphinidenes complexes from their corresponding 7-phosphanorbornadiene complexes, probably due to coordination of the nitrogenous lone pair to the copper(I) ion.

The generation of terminal phosphinidene complexes without the explicit addition of a trapping agent is yet another example where the generation of a terminal phosphinidene complex by thermal means and by the addition of copper(I) chloride as a catalyst leads to vastly different outcomes. In the absence of copper(I) chloride, more forcing conditions are required for decomposition of 7-phosphanorbornadiene complexes and under these conditions, two different cyclopolyphosphanes are formed from the chromium(0) precursor. These two results are summarised schematically below.

Scheme 1.48 Oligomerization of Terminal Phosphinidene Complexes

Interestingly, when the complexing metal is changed to the other members of the Group VI triad, the reaction pathway is drastically different.⁸⁸ In line with the stabilising potential of the metal carbonyl, the chromium analogue decomposes at a much quicker rate, and favours the formation of the tetramer, as compared to the formation of the trimer for tungsten, largely in part to the greater steric restriction imposed by tungsten. Conversely, the molybdenum variant decomposes slowly (contrary to what is expected on the basis of bond strengths), forming a myriad of paramagnetic compounds.

1.3.2.2 Cycloaddition

Being electrophilic in nature, it is natural that these electron deficient species react with electron rich moieties. Accordingly, one characteristic reaction of terminal phosphinidene complexes is their [2+1] cycloaddition with alkynes and alkenes, forming phosphirene and phosphirane complexes respectively.

The first instance of this reaction was reported in 1982 by Mathey and co-workers.³³ Here, the authors heated the appropriate 7-phosphanorbornadiene complexes in the presence of alkynes to form the corresponding phosphirene complexes.

Scheme 1.49 [2+1] Cycloaddition of Terminal Phosphinidene Complexes and Alkynes

As mentioned in a previous section, when generated thermally, the reaction was found to be first-order in concentration of the 7-phosphanorbornadiene complex and zero-order in concentration of trapping agent.³⁹ This observation was paralleled when terminal phosphinidene complexes were generated using 3*H*-benzophosphepines.⁵⁸

The addition to alkenes proved to be a bit more problematic. This is due to the fact that the resultant trapping products, the phosphirane complexes, are also precursors to terminal phosphinidene complexes by undergoes a [2+1] retroaddition. Mathey and co-workers proposed the solution to this stumbling block in 1984.⁴⁰ The trick was to decompose the 7-phosphanorbornadiene complexes with copper(I) chloride. As the decomposition temperature is drastically reduced to around 60 °C, the [2+1] retroaddition is suppressed.

Scheme 1.50 [2+1] Cycloaddition of Terminal Phosphinidene Complexes and Alkenes

It is critical to note at this juncture that stereochemistry around the olefin is retained, suggesting that the reaction is concerted. The addition of terminal phosphinidene complexes to olefins (*para*-substituted styrenes in this case) have allowed for a quantification of their reactivity. Lammertsma and co-workers have performed studies to determine Hammett reaction constants of various phosphinidene complexes.⁸⁹ The reported values are closely aligned with that of “free” carbenes, providing further evidence of the electrophilicity of these species.

Selectivity of [2+1] cycloaddition (if any) appears to be governed by steric factors, with the phosphinidene complex preferring to project the bulky tungsten complexing group away from the side with a larger steric bulk. This can be seen in the cycloaddition between phenylphosphinidene pentacarbonyltungsten(o) complex and *cis*-but-2-ene, with the *anti*-isomer being formed as the major product.^{89c} In the same publication, Lammertsma and co-workers also reported that in cases with more than one carbon-carbon double bond, the phosphinidene complex selectively adds to the less sterically demanding, still with the *anti*-isomer formed to a larger extent as compared to the *syn*-isomer.

Scheme 1.51 Olefin Selectivity In Cycloadditions With Terminal Phosphinidene Complexes

If a carbon-carbon triple bond is present, but addition *via* a direct [2+1] cycloaddition is hindered by factors such as geometrical constraints, unique reaction sequences can be developed. Mathey and co-workers observed this by incorporating the alkyne moiety onto the phosphinidene substituent in a geometrically unfavourable arrangement.⁹⁰ A cycloaddition, forming a benzoannulated phosphole, *via* a zwitterionic intermediate. An electrophilic character on the carbon atom induces the incorporation of an aryl moiety (a solvent unit in this case) by an electrophilic aromatic substitution-type pathway.

Scheme 1.52 Prevention of [2+1] Cycloaddition With Alkynes by Geometrical Constraints

When conjugated dienes are used as trapping agents, phospholene complexes are formed. This addition takes place in two steps. Firstly, a [2+1] addition takes place and the initial products are the expected diastereomeric

isomers of 2-vinylphosphirane complexes. The products are then converted to the 3-phospholene complex upon heating. Computational studies undertaken by Lammertsma and co-workers show that this conversion takes place *via* a [1,3]-sigmatropic rearrangement.⁸³

Scheme 1.53 Formation of Vinylphosphirane Complexes and Further Conversion Into Phospholene Complexes

The “trapping” of terminal phosphinidene complexes need not be restricted to an intermolecular conversion. When the phosphinidene substituent contains an unsaturated bond, it can be trapped intramolecularly. This was exploited by Mathey and co-workers to form a novel bicyclic structure, incorporating both a phosphirane and phospholane unit.⁹² This intramolecular process occurs appreciably faster than an intermolecular process and the phosphinidene complex was unable to be trapped by the addition of an external trapping agent.

Scheme 1.54 Intramolecular [4+2] Cycloaddition of Terminal Phosphinidene Complexes With Olefins

Lammertsma and co-workers have studied a structural analogue of these strained systems.⁹³ The intramolecular addition of an aminophosphinidene tetracarbonyliron(0) complex onto carbon-carbon double bonds or triple bonds yields strained bicyclic frameworks. This addition is reversible, with

the phosphirane and phosphirene complexes undergoing retroaddition readily, even at room temperature, as evidenced by trapping in neat phenylacetylene. The facile reversibility is probably due to the strain in the bicyclic system and the diminished energy barrier for the retroaddition due to interaction of the nitrogen lone pair with the vacant orbital on the terminal phosphinidene complex. As expected, a change in the number of carbons in the tether has the potential to alter the reaction pathway due to differences in ring strain.

Scheme 1.55 Reversible Intramolecular [4+2] Cycloaddition of Terminal Phosphinidene Complexes With Olefins and Subsequent Trapping With Phenylacetylene

This addition is not restricted solely to carbon-based unsaturated bonds. Indeed, terminal phosphinidene complexes add to polar, unsaturated bonds such as aldehydes and aldimines, forming the corresponding oxaphosphirane and azaphosphirane complexes respectively.⁹⁴

Scheme 1.56 Cycloaddition of Bulky Terminal Phosphinidene Complexes With C=O and C=N Double Bonds

It must be noted that this reaction pathway is viable only when the phosphorus substituent has an extreme steric bulk. When smaller substituents are used, the initial three-membered ring is not sufficiently stabilised, and subsequent insertions take place. When phenylphosphinidene

pentacarbonyltungsten(o) is used, the insertion of another imine unit forms a diastereomeric mixture of five-membered rings.⁹⁵ When methylphosphinidene pentacarbonyltungsten(o) is used, in addition to the formation of the five-membered ring, insertion of another phosphinidene unit can take place, forming a four-membered ring.⁹⁶

Scheme 1.57 Cycloaddition of "Normal" Terminal Phosphinidene Complexes With C=N Double Bonds

When α,β -conjugated imines and ketones are used as trapping agents, the reaction mixture exclusively yields the [4+1] cycloadducts.^{40, 97}

Scheme 1.58 Cycloaddition of Terminal Phosphinidene Complexes With α,β -Unsaturated C=O and C=N Double Bonds

Harnessing the above reaction with α -enones, when a chloro group is used as the phosphinidene substituent, dehydrohalogenation of the intermediate oxaphospholene complex takes place in the presence of a N-methylimidazole, forming a 2-phosphafuran complex.⁹⁸ This species shows moderate aromaticity, and while it is stable at room temperature, its high reactivity precluded its isolation. The structure was verified by a series of trapping experiments.

Scheme 1.59 Synthesis of 2-Phosphafuran Tungsten(0) Complex

The facile [2+1] cycloaddition is not limited to organic substrates. Phosphaalkynes, when used as trapping agents, give the expected 1,2-diphosphirene complexes.⁹⁹ The instability of this species rendered isolation impossible. Upon standing for four weeks at room temperature, a series of ring openings, dimerization and rearrangements takes place, forming a fused, tricyclic structure, which was characterised by X-ray crystallographic analysis.

Scheme 1.60 Trapping of Terminal Phosphinidene Complexes With Phosphaalkynes

Unsaturated bonds containing metals also function in a similar vein. A tungsten carbyne complex has been used, giving a metallaphosphirene product, which proved to be fairly stable.¹⁰⁰ The results with tungsten carbene complexes proved to be less successful, with the three-membered ring proving to be unstable and highly reactive, losing the tungsten moiety under reaction conditions, yielding a phosphaalkene complex, which dimerizes in a head-to-head fashion.¹⁰¹

Scheme 1.61 Trapping of Terminal Phosphinidene Complexes With Tungsten Carbyne & Carbene Complexes

Metal-metal double bonds have also been used as trapping agents, forming a three-membered inorganic ring.¹⁰²

Scheme 1.62 Cycloaddition of Terminal Phosphinidene Complexes With Rh=Rh Double Bonds

1.3.2.3 Insertion

While the chemistry of electrophilic terminal phosphinidene complexes is richest for cycloadditions, insertions of these reactive species into various bonds still forms a staple portion of the synthetic repertoire.

The earliest examples involving these insertions are that into oxygen-hydrogen bonds of alcohols or water, and the nitrogen-hydrogen bond of amines.^{33, 103} In both cases, conversion into their corresponding secondary phosphane complexes was fairly quantitative, especially in cases where pentacarbonyltungsten(o) was used as a complexing group. This is yet another example where the stabilising effect of the complexing group is evident; in their free state, these phosphanes are inherently unstable.

Scheme 1.63 Insertion of Terminal Phosphinidene Complexes Into A-H Bonds

In 2016, Mathey & Duan, through a theoretical study, have shed some light on a possible mechanism using methylphosphinidene pentacarbonyltungsten(o) and water as representative examples.¹⁰⁴

Apparently, this reaction proceeds *via* the formation of a Lewis acid-base adduct with the oxygen lone pair and the vacant p orbital of phosphorus. The [1,2] shift of hydrogen from oxygen to phosphorus gives the secondary phosphane complex. A transition state was located 11.4 kcal mol⁻¹ above the water adduct, a finding consistent with the reaction conditions. It is likely that a similar mechanism is at play when amines and alcohols are utilised.

Scheme 1.64 Mechanism Of Terminal Phosphinidene Complex Formation Into O-H Bond of Water

These secondary phosphane complexes have some synthetic potential and their formation is not purely an academic exercise. The secondary phosphane complexes are weakly acidic and can be deprotonated by bases such as potassium *tert*butoxide or *n*-butyllithium and reacted with electrophiles such as methyl iodide or benzophenone, alkylating the phosphide or forming the expected alcohol respectively. In addition, when aniline is used as the trapping agent, the resultant secondary amine moiety can be converted to the halide by reaction with dry hydrogen halides at room temperature.

Scheme 1.65 Subsequent Functionalization of Insertion Products

A combination of these two reactions were utilised in the synthesis of 1-chlorophosphirane pentacarbonyltungsten(o) with no ring substitution.¹⁰⁵

Starting with 7-(β -chloroethyl)-7-phosphanorbornadiene complex, the phosphinidene complex was generated and trapped with aniline. Deprotonation of the weakly acidic hydrogen is performed by the addition of *n*-butyllithium. The phosphide cyclises to form the aminophosphirane complex. Addition of dry hydrogen chloride yields the desired phosphirane complex.

Scheme 1.66 Synthesis of 1-Chlorophosphirane Tungsten(0) Complex

Terminal phosphinidene complexes have been formally added across the hydrogen-hydrogen bond of dihydrogen.¹⁰⁶ The reaction yields the primary phosphine complex, though the mechanism is rather complex. On the basis of DFT calculations, it seems that dihydrogen is added across the phosphorus-tungsten bond, followed by homolysis of the tungsten-hydrogen bond. Dimerization of the resultant phosphorus radical yields the dissecondary diphosphane. Hydrogenation of the weak phosphorus-phosphorus single bond gives the primary phosphine complex.

Scheme 1.67 Formal Insertion of Terminal Phosphinidene Complex Into Dihydrogen

Addition into silicon-hydrogen bonds also takes place. Serenberg and co-workers, utilising a stable, cationic phosphinidene complex, was able to cleave a silicon-hydrogen bond, forming a secondary silylphosphane complex.¹⁰⁷ Computational studies revealed that the reaction was concerted

with a triangular transition state. It is likely that the hydridic character of the hydrogen atom and partial positive charge of silicon atom (Mulliken charges: H = -0.118; Si = +0.265) provides the driving force for the reaction to take place.

Scheme 1.68 Insertion of Cationic Phosphinidene Complex Into Si-H Bonds

Mathey and co-workers have also reported the insertion of terminal phosphinidene complexes into boron-hydrogen bonds of phosphine- or amine-boranes.¹⁰⁸ It is likely that the reaction pathway is fairly analogous in nature.

Scheme 1.69 Insertion of Terminal Phosphinidene Complex Into B-H Bonds

The reaction is different when copper(I) chloride is used as a catalyst. At these lower generating temperatures, insertion into the boron-hydrogen bond does not take place due to the higher activation barrier. Dimerization is the preferred pathway, forming diphosphene complexes. Nucleophilic attack of the negatively charged boron then forms the disubstituted diphosphane complex.¹⁰⁶

Scheme 1.70 Formation of Dissecondary Diphosphane Complexes

The insertion of terminal phosphinidene complexes into boron-oxygen bonds has also been effected. Ng and Mathey have reported the insertion of a range of phosphinidene complexes into boronic acids.¹⁰⁹ Mechanistic studies reveal that after the initial insertion, attack of a base on the trivalent boron atom causes the boronic acid substituent to migrate to the phosphorus with a concomitant loss of a hydroxide moiety. Hydrolysis completes the reaction sequence.¹¹⁰ This reaction does not work with alkyl boronic acids.

Scheme 1.71 Insertion of Terminal Phosphinidene Complexes Into B-O Bonds of Boronic Acids

In 2016, it was reported that terminal phosphinidene complexes could be inserted into the phosphorus-hydrogen bond of secondary phosphine oxides.¹¹⁰ This reaction does not work when secondary phosphines or secondary phosphine tungsten(o) complexes are used. DFT studies revealed that the secondary phosphine oxide tautomerized into a phosphinous acid, which interacts with the electron deficient phosphinidene complex through the oxygen atom, forming a Lewis acid-base adduct. The transformation is completed by a [1,2] hydrogen shift, similar to what is observed in the

insertion of water and alcohols. An isomerization then takes place, giving the formal addition product.

Scheme 1.72 Formal Insertion of Terminal Phosphinidene Complexes Into P-H Bond of Secondary Phosphine Oxides

Of course, from a synthetic standpoint, the most useful insertions are insertions into carbon-hydrogen bonds. The formation of phosphorus-carbon bonds plays a pivotal role in the synthesis of organophosphorus molecules.¹¹¹ The earliest example involves the insertion into the carbon-hydrogen bond of ferrocene.¹¹² This reaction has not yet been transposed to other isolated aromatic rings such as thiophene, furan or pyrrole. The reaction with ferrocene works in part due to the negative charge associated with the carbon-hydrogen bond.

Scheme 1.73 Insertion of Terminal Phosphinidene Complexes Into C-H Bond of Ferrocene

With methyl ketones, phosphinidene complexes exhibit a formal insertion into an α -carbon-hydrogen bond.¹¹³ This reaction has been shown to work with acetone and acetophenone. The reaction can be rationalised by addition

onto the carbon-carbon double bond of the enol form, followed by ring opening of the resultant phosphirane complex.

Scheme 1.74 Insertion of Terminal Phosphinidene Complexes Into α -C-H Bond of Enolizable Ketones

Similar to what was observed by Cowley and co-workers, having a carbon-hydrogen bond in close proximity to the reactive phosphinidene centre would allow for an insertion to take place. This concept was expanded by Mathey and co-workers in their insertion into azobenzene.¹¹⁴

Scheme 1.75 Insertion of Terminal Phosphinidene Complexes Into an *ortho*-C-H Bond of Azobenzene

The same group further exploited this by an intramolecular carbon-hydrogen insertion. By their judicious choice of using biaryls or biheteroaryls as a phosphinidene substituent, insertion into a proximal bond allows for the formation of a wide range of annelated phosphole complexes.¹¹⁵ Of special mention is when 2-(3-thienyl)phenyl is used as a substituent. In theory, the insertion could take place at two carbons, namely the α and β' positions. The insertion takes place exclusively at the α carbon-hydrogen bond, in line with the higher negative charge at α -carbons of thiophene.¹¹⁶ This representative example is shown below.

Scheme 1.76 Selective Intramolecular Insertion of Terminal Phosphinidene Complexes Into α -C-H Bond of Thiophene

The insertion of terminal phosphinidene complexes into strained bonds also deserves some mention. Insertion of phosphinidene complexes into a carbon-nitrogen bond of aziridine was reported by Mathey and co-workers.¹¹⁷ As expected, the insertion takes place at the less sterically encumbered carbon-nitrogen bond, forming the desired four-membered ring, which were characterised as a mixture of diastereomers. In the same publication, the insertion into epoxides was attempted. The results were less successful, forming a mixture of phosphirane and dioxaphospholene complexes with the expected oxaphosphetane complex being postulated as an intermediate.

Scheme 1.77 Insertion of Terminal Phosphinidene Complexes Into Strained Rings

Insertion into the carbon-oxygen bond of epoxides and successful isolation of 1,2-oxaphosphetane complex was finally achieved by Streubel and co-workers in 2014.¹¹⁸ Utilization of a phosphinidenioid complex with a bulky

substituent allowed for the kinetic stabilization of the expected 1,2-oxaphosphetane complexes.

Scheme 1.78 Insertion of Phosphinidenoid Complexes Into Epoxides

Phosphirene complexes have also been used as substrates for insertions into strained rings. 2-Alkynylphosphirene complexes were converted into 1,2-diphosphete complexes by insertion into the weaker phosphorus-carbon bond; conjugation to the alkyne fragment causes bond elongation and no reaction is observed in the absence of this group.¹¹⁹ Unexpectedly, no [2+1] cycloaddition to the triple bond was observed.

Scheme 1.79 Insertion of Terminal Phosphinidene Complexes Into P-C Bonds of Phosphirene Complexes

A final example concerns the addition of a phosphinidene complex into a metal-carbon bond. When reacted with an extremely strained nickel cluster, insertion into a nickel-carbon bond yielded a metallophosphete complex.¹²⁰

Scheme 1.80 Insertion of Terminal Phosphinidene Complexes Into Strained Ni-C Bonds

1.3.2.4 Phospha-Wittig

Terminal phosphinidene complexes are electrophilic in nature. With the vacant p orbital, they have the ability to function as Lewis acids, a feature we covered previously when looking at the insertion of terminal phosphinidene complexes into water. Upon coordination, a negative charge (at least formally) is present on the phosphorus atom.

Leveraging this, Mathey reported on the cheletropic elimination of 7-phosphanorbornadiene complexes in the presence of a Lewis base such as amines or phosphines.¹²¹ The decomposition takes place at ambient temperatures, or at slightly elevated temperatures (20 °C to 40 °C). The drastically milder conditions seem to be due to an attack of the Lewis base on the bridgehead phosphorus atom. It has been reported that quarternization of a phosphorus bridgehead causes it to collapse.¹²²

Scheme 1.81 Lewis Base-Catalysed Decomposition of 7-Phosphanorbornadiene Complexes

When tributylphosphine is used as the Lewis base, phosphoranylidene phosphane complexes are formed. These compounds are

extremely unstable and hence, usually generated *in situ* and utilised directly. In the $^3\text{P}\{^1\text{H}\}$ NMR spectrum, both phosphorus atoms show coupling constants of around 400 Hz, consistent with a one-bond phosphorus-phosphorus coupling. One crystal structure was reported, with a phosphorus-phosphorus bond length of 2.156(2) Å, indicating that a zwitterionic formulation with a single bond was predominant.³⁴ In addition, the phosphorus-tungsten coupling constant is unusually low, indicative of a negative charge at the phosphinidene phosphorus atom.¹²³

Scheme 1.82 Synthesis of Phospha-Wittig Reagents

These reactive compounds react readily with aldehydes, yielding phosphaalkene complexes. Problems with isolation obliged the authors to trap these reactive species *in situ* with alcohols or 2,3-dimethylbutadiene.

Scheme 1.83 Reaction of Phospha-Wittig Reagents With Aldehydes

Alkylation can take place at the phosphinidene phosphorus atom. This reaction has found utility in the synthesis of phosphorus heterocycles. When the phosphorus substituent is an alkylchloride, intramolecular alkylation takes place.¹²⁴ Attack of the chloride ion on the phosphorus cleaves the phosphorus-phosphorus bond, forming tributylphosphine and a 1-chlorophosphacycle. A representative example is shown below in the synthesis of 1-chlorophospholane complex.

Scheme 1.84 Intramolecular Substitution of Alkyl Chlorides With Phospha-Wittig Reagents

1.3.3 Nucleophilic Phosphinidene Complexes

The chemistry and reactivity of nucleophilic phosphinidenes has not been explored to a great extent. The key reactions will be covered in this section.

The most characteristic reaction of nucleophilic phosphinidene complexes is the addition to aldehydes and ketones, forming phosphoalkenes in the so-called “phospha-Wittig” reaction. This was demonstrated by Schrock in the reaction of a linear tantalum phosphinidene with aldehydes.⁷⁰ The phosphoalkenes are unstable when smaller substituents are used, and isolated as their [2+2] dimers, or as their Diels-Alder adducts after cycloaddition with cyclopentadiene. If a substantial steric bulk is present, the phosphoalkenes, stabilised kinetically, are isolable.

Scheme 1.85 Phospha-Wittig Reaction of Tantalum Phosphinidene Complexes and Aldehydes

This reaction also works with bent phosphinidene complexes. Stephan, in 1995, reported the phospha-Wittig reaction with benzophenone and isophthalaldehyde.¹²⁵ This reaction does not work with enolizable carbonyl functionalities; the basicity of the phosphinidene complex was sufficient to generate the oxygen-bound enolate complex.

Scheme 1.86 Phospha-Wittig Reaction of Phosphinidene Zirconium Complexes With Bis-aldehydes

Nucleophilic phosphinidenes, with a formal oxidation state of +3, is synthetically equivalent to $[RP]^{2-}$. It is no surprise that they react with alkyl and alkenyl halides to yield a range of phosphorus heterocycles.¹²⁵ The reaction with 1,2-dichloroethane and 1,2-(chloromethyl)benzene yields the expected phosphirane and 3-benzophospholene respectively.

Scheme 1.87 Alkylation of Zirconium Phosphinidene Complexes Forming Phosphorus Heterocycles

Substitution of benzoannulation with a carbon-carbon double bond changes the reaction pathway drastically. Instead of the expected 3-phospholene, the intermediate phosphide undergoes a SN_2' -type reaction, forming 2-vinylphosphirane and a zirconium-chlorine bond. This result was verified by using a carbon-carbon triple bond, forming the allenic-phosphirane.

Scheme 1.88 Alkylation of Zirconium Phosphinidene Complexes Forming Phosphiranes

When the two halides are found on the same carbon atoms (such as methylene chloride or chloroform), phosphalkenes are generated.

Scheme 1.89 Alkylation of Zirconium Phosphinidene Complexes and Subsequent Phosphaalkene Formation

Alkynes add to Stephan's zirconium phosphinidene complex to form metallophosphetes.¹²⁶ This presumably takes place through initial π -coordination of the alkyne to zirconium, followed by [2+2] cycloaddition. This process is reversible and can generate the starting phosphinidene complex in the presence of a stabilising group such as trimethylphosphine.

Scheme 1.90 [2+2] Cycloaddition of Zirconium Phosphinidene Complexes With Alkynes

The situation is similar when a ruthenium phosphinidene complex, reported by Lammertsma, is utilised.^{73a} However, upon formation of a metallophosphete, an insertion into a vicinal carbon-hydrogen bond takes place, along with a concurrent hydrogen transfer onto the olefin, yielding a phosphaaallyl complex.

Scheme 1.91 Formation of Metallophosphete and Subsequent C-H Insertion

The reaction with unsaturated carbon-carbon bonds is different with Hillhouse's nickel phosphinidene complex.¹²⁷ Reaction with ethylene gives an intermediate [2+2] cycloadduct, which breaks down reductively to yield a phosphirane.

Scheme 1.92 [2+2] Cycloaddition of Nickel Phosphinidene Complexes With Alkenes

With alkynes, the reaction is once again different. With phenylacetylene, the resultant phosphirene is bound to the nickel in a η^2 fashion.¹²⁸ It is proposed that the reaction is similar to what is seen with olefins. Upon reductive elimination, the carbon-carbon double bond is intercepted by nickel. The carbon-carbon bond length of 1.392(7) Å is comparable to the same bond in phosphirenes.¹²⁹

Ar = 2,6-Mes-C₆H₃

Scheme 1.93 [2+2] Cycloaddition of Nickel Phosphinidene Complexes With Alkynes

Hey-Hawkins has reported the double insertion of acetone into the tantalum-phosphorus bond of a tantalum phosphinidene complex to give the O-bound tantalum complex.¹³⁰ The mechanism is not detailed, but could involve the interception of an intermediate in the phospha-Wittig reaction by another molecule of acetone, followed by coordination to the metal centre.

Ar = 2,4,6-iPr-C₆H₂

Scheme 1.94 Double Insertion of Acetone Into Tantalum Phosphinidene Complexes

1.4 Conclusion

The myriad of reactions that have been highlighted represent a small proportion of what exists in the chemical literature where phosphorus is concerned. It is evident that within the realm of low-valent phosphorus, there is much to be explored. New modes of activation and different ligand scaffolds remain to be discovered. That is the purpose of this dissertation and my exploration of the subject matter will be covered in the following chapters.

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2

Generation and Trapping of Superelectrophilic Phosphinidene Complex $[\text{F}_3\text{C-PW}(\text{CO})_5]$

DFT studies show that the trifluoromethylphosphinidene tungsten(o) complex is the most electrophilic species described to date; its LUMO is 0.30 eV lower in energy than the chloro analogue. It is generated from the reaction of DMAD and the 1-trifluoromethylphosphole pentacarbonyltungsten(o) complex. It reacts with alkynes but only electron rich alkenes. The instability of phosphirane complexes derived from electron poor alkenes shows the importance of backbonding from phosphorus to the π^* orbitals of the olefin.

2.1 Introduction

Terminal phosphinidene complexes have an extremely deep and interesting chemistry.¹ Of these, the electrophilic species has the widest synthetic utility in light of the plethora of reactions that these transient species can undergo. Their reactivity is governed by the electrophilicity of the electron deficient phosphorus atom and they tend to react with electron rich species. It follows accordingly that in order to heighten the reactivity of the system, the electrophilicity of the phosphorus atom needs to be boosted. There are two ways this can be accomplished.

The first way is to increase the electron withdrawing capability of the metal. This is not a strategy that would be easy to accomplish. Most of the metal-based complexing groups used to stabilise the phosphinidene are from the

Group VI pentacarbonyl triad. It has been shown by Lammertsma and co-workers that the metal has little impact on the electronic properties of the phosphinidene center.² Rather, it is the identity of the ligands that has the most profound impact. Already having five extremely π -accepting carbonyl ligands on the metal centre, it would be hard to fathom a method to graft a larger number of carbonyl groups or to find a ligand with a greater π -withdrawing ability.

The second strategy, to modulate the electrophilicity of the phosphinidene by modifying the phosphorus substituent, is a much more logical approach. An obvious choice would be to graft a halogen atom on to the phosphinidene in light of their higher electronegativities. Mathey and co-workers have explored this previously by their attempted generation of fluorophosphinidene pentacarbonyltungsten(0).³ Upon treatment of the 1-chloro-3,4-dimethylphosphole pentacarbonyltungsten(0) complex **1** with potassium fluoride in the presence of 18-crown-6, an exchange of the halogen atom takes place, yielding 1-fluoro-3,4-dimethylphosphole pentacarbonyltungsten(0) **2**.

Scheme 2.1 Synthesis of 1-Fluorophosphole Tungsten(0) Complex

This phosphole complex turned out to be extremely reactive. Upon standing, the phosphole complex dimerizes, forming the endo dimer.

Scheme 2.2 Dimerization of 1-Fluorophosphole Complex

This reactivity was exploited by its $[4+2]$ cycloaddition with DMAD. The reaction was complete after 2 hours at 80 °C with a stoichiometric quantity of DMAD, a huge rate increase when compared to the phenyl analogue (24 hours, 85 °C, 3 equivalents of DMAD).

Scheme 2.3 $[4+2]$ Cycloaddition Between 1-Fluorophosphole Tungsten(0) Complex and DMAD

Unfortunately, its corresponding 7-phosphanorbornadiene complex **3** did not parallel the immense reactivity of phosphole complex **2**. In an attempt to generate the terminal phosphinidene complex **4** and trap it with diphenylacetylene, **3** was heated to 160 °C in the presence of copper(I) chloride but decomposition *via* cheletropic elimination did not take place.

Scheme 2.4 Attempted Generation of Fluorophosphinidene Tungsten(0) Complex

This result was rather surprising, considering that “normal” substituents on the 7-phosphanorbornadiene complex framework allow for its decomposition at around 110 °C or around 55 °C in the presence of copper(I) chloride.

The problem associated with the decomposition of **3** was a consequence of the short phosphorus-fluorine bond, stabilising the system. In an attempt to destabilise the bicyclic framework, a poorer complexing group was necessary. Frenking and co-workers have performed a computational study on phosphine complexes of the Group VI metal carbonyl triad.⁴ They found that the phosphorus-metal bond dissociation energies are strongest for phosphorus-tungsten (43.8 kcal mol⁻¹), weakest for phosphorus-molybdenum (37.9 kcal mol⁻¹) with phosphorus-chromium coming in the middle (41.2 kcal mol⁻¹).

The utilization of pentacarbonyl molybdenum(0) posed a new problem due to its incompatibility with sulfuryl chloride, the chlorinating agent in the original synthesis of 1-chlorophosphole pentacarbonyltungsten(0) complex **1**. Mathey and co-workers proposed a new route to **5**, which was a direct fluorination of a phospholide complex with a cationic fluorine source.⁵

Scheme 2.5 Synthesis of 1-Fluorophosphole Molybdenum(0) Complex

The molybdenum analogue **5** proved to be much less reactive than **2**. Four equivalents of DMAD were necessary to prevent self-dimerization of **5** into **6**.⁶

Scheme 2.6 Reactivity of 1-Fluorophosphole Molybdenum(0) Complex

7 proved to be a precursor of the superelectrophilic terminal phosphinidene complex **8**. When heated to 120 °C in the presence of diphenylacetylene and 2,3-dimethylbutadiene, the corresponding phosphirene and 3-phospholene complexes were formed.

Scheme 2.7 Generation and Trapping of Fluorophosphinidene Complex

In 2009, Mathey and co-workers revealed that despite the higher electronegativity of fluorine, chlorophosphinidene pentacarbonyltungsten(o)

is a much more electrophilic species than the fluoro variant.⁷ DFT studies showed that due to interaction with chlorine atom, the HOMO, corresponding to the phosphorus lone pair, is stabilised and the empty p orbital at phosphorus, the LUMO, is destabilised. The destabilization is much weaker than the fluorophosphinidene complex as the phosphorus-chlorine bond (2.107 Å) is much longer than the phosphorus-fluorine bond (1.632 Å). This results in the chlorophosphinidene complex being the most electrophilic species.

The chlorophosphinidene complex could have been generated from the corresponding 7-chloro-7-phosphanorbornadiene complex **9**, which in turn is synthesized from the 1-chlorophosphole pentacarbonyltungsten(o) complex **1** and DMAD.

Mathey and co-workers have previously attempted the synthesis of **9** but all only decomposition was observed.³

Scheme 2.8 Attempted Generation of 7-Chloro-7-Phosphanorbornadiene Tungsten(0) Complex

Later on, based on the working hypothesis that the 7-chloro-7-phosphanorbornadiene **9** was being formed, but decomposes at under the reaction conditions, the solution to obtaining the phosphinidene complex was to react **1** with DMAD and the trapping agent in a one-pot reaction.

Scheme 2.9 Generation of Chlorophosphinidene Tungsten(0) Complex

The existence of chlorophosphinidene pentacarbonyltungsten(o) **10** was verified on the basis of trapping with diphenylacetylene and 2,3-dimethylbutadiene, forming the corresponding phosphirene and 3-phospholene complexes respectively.

Scheme 2.10 Trapping of Chlorophosphinidene Tungsten(0) Complex

We decided to try and synthesize a terminal phosphinidene complex that was even more electrophilic in nature and thought that the trifluoromethyl substrate might be suitable. This chapter highlights our attempts at generation and trapping of these potentially superelectrophilic terminal phosphinidene complexes.

2.2 Results and Discussion

In order to verify that this was feasible, we checked the electronic structure of trifluoromethylphosphinidene pentacarbonyltungsten(o) **11** by DFT at the

RB3PW91/6-31+G(d,p)-LanL2DZ(W) level.⁸ The optimised structure is shown below.

Figure 2.1 Optimised Structure of Trifluoromethylphosphinidene Pentacarbonyltungsten(0)

The structure is fairly comparable to what is observed with other phosphinidene complexes. The HOMO and LUMO shapes are unexceptional, with the phosphorus lone pair being seen in the HOMO, and the vacant p orbital being present in the LUMO. They can be seen in Figure 2.2.

Figure 2.2 HOMO (Left) and LUMO (Right) of Trifluoromethylphosphinidene Tungsten(0) Complex

While the structure and frontier orbitals seem uninteresting, the computation revealed something worth mentioning. The LUMO, at -4.54 eV, is 0.30 eV lower in energy than that of chlorophosphinidene pentacarbonyltungsten(o). Similarly, the HOMO, at -6.97 eV, is 0.12 eV lower in energy. These results show that trifluoromethylphosphinidene pentacarbonyltungsten(o) complex **11** is much more electrophilic than its chloro counterpart. We were tempted to generate **11** and check if its enhanced electrophilicity would allow for new or improved reaction pathways.

We explored possible routes to terminal phosphinidene complex **11** and the route of choice that represented the best chance of generation was *via* the 7-trifluoromethyl-7-phosphanorbornadiene complex **12**. This necessitated a synthesis of the 1-trifluoromethylphosphole pentacarbonyltungsten(o) complex **13**.

Scheme 2.11 Retrosynthetic Analysis Towards The Generation of Trifluoromethylphosphinidene Tungsten(0) Complex

Synthesis of phosphole complex **13** could have been achieved by one of two routes. The nucleophilic attack of a trifluoromethyl anion (or its synthon) on the 1-cyanophosphole pentacarbonyltungsten(o) complex **14** or the electrophilic attack of a trifluoromethyl cation (or its synthon) by the tungsten(o) phospholide complex **15**.

Scheme 2.12 Two Routes Towards The Synthesis of 1-Trifluoromethylphosphole Tungsten(0) Complex

Route 1 could have been achieved by the use of trifluoromethyltrimethylsilane (Ruppert-Prakash reagent) in the presence of a Lewis base, usually TBAF, caesium fluoride, potassium *tert*butoxide, potassium acetate, potassium carbonate or tris(*tert*butyl)phosphine.⁹ These compounds were not compatible with the cyano functionality, though typically, only sub-stoichiometric quantities were required.

We pursued route 2 because of the easy availability of phospholide complex **15**. A search for synthons of the trifluoromethyl cation led us to Togni's reagents.¹⁰ Togni's reagent I was synthesized as a one-pot reaction according to an established literature protocol.¹¹

Scheme 2.13 Synthesis of Togni's Reagent I

This procedure relies on an “umpolung” of the trifluoromethyl group, converting the nucleophilic trifluoromethyl moiety in trifluoromethyltrimethylsilane to the electrophilic trifluoromethyl group in hypervalent iodine reagent **16**.

Having an electrophilic trifluoromethyl source in hand, we attempted to synthesize trifluoromethylphosphole complex **13**. Starting from a THF solution of 1-phenyl-3,4-dimethylphosphole **17**, the exocyclic phosphorus-carbon bond was cleaved with a reactive metal, lithium in our case, forming one unit of lithium phospholide **18** and one equivalent of phenyllithium. Phenyllithium was destroyed by the addition of *tert*butylchloride and warming to 65 °C for 1.5 hours. Phospholide complex **15** was formed by the addition of tungsten(0) hexacarbonyl, followed by stirring at room temperature for 14 hours.

Scheme 2.14 Synthesis of Tungsten(0) Phospholide Complex

The synthesis of trifluoromethylphosphole complex **13** was completed with the addition of **15** to a THF solution of **16** at 0 °C.

Scheme 2.15 Synthesis of 1-Trifluoromethylphosphole Tungsten(0) Complex

The reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR and the appearance of a quartet with tungsten satellites at +27 ppm ($^2J_{\text{P-F}} = 70.2 \text{ Hz}$, $^1J_{\text{P-W}} = 235 \text{ Hz}$) was indicative that trifluoromethylphosphole complex **13** was formed successfully. Purification by column chromatography over silica gave **13** as a pale yellow solid in 21% yield. Crystals suitable for X-ray crystallographic analysis were grown from DCM/Hex at room temperature and its molecular structure can be seen in Figure 2.3.

Figure 2.3 X-ray Crystal Structure of 1-Trifluoromethylphosphole Tungsten(0) Complex **13**. Main Distances (Å) and Angles (°): P1-W1 2.4678(16), P1-C6 1.878(8), P1-C7 1.780(6), P1-C12 1.787(8), C7-C8 1.331(9), C8-C10 1.500(9), C10-C12 1.320(9); C7-P1-C12 91.5(3), C7-P1-C6 101.4(3), C12-P1-C6 100.1(3)

The phosphole ring is quasi planar, with a slight puckering of the phosphorus atom in an envelope conformation. The angle between the C12-P1-C7 and C7-C8-C10-C12 planes is 3.44° . The C7-C8 (1.331(9) Å) and C10-C12 (1.320(9) Å) bond lengths are comparable, but much shorter than the C8-C10 bond length (1.500(9) Å). The alternate single and double bonds hint at a degree of anti-aromaticity in the phosphole ring. This is somewhat expected as a strongly electron withdrawing moiety on the phosphorus atom should leave it with a slight partial positive charge.

With the successful synthesis and isolation of phosphole complex **13**, its reaction with DMAD was explored in an attempt to synthesize 7-trifluoromethyl-7-phosphanorbornadiene tungsten(0) complex **12**. Heating a toluene solution of **13** and DMAD to 80°C for 18 hours led to a drastic

decrease in signal-to-noise ratio of the phosphole complex, and no new low-field signal was observed. It seemed that the $[4+2]$ cycloaddition was indeed taking place, but the 7-phosphanorbornadiene skeleton was too unstable, and the subsequent cheletropic elimination was taking place.

Scheme 2.16 Attempted Synthesis of 7-Trifluoromethyl-7-Phosphanorbornadiene Tungsten(0) Complex

Following the strategy reported in 2009 by Mathey and co-workers, a one-pot generation and trapping procedure was performed, with the trapping agent being added to the DMAD reaction mixture.⁷ This protocol allows for the formation and cheletropic elimination to take place in the same step, forming the phosphinidene complex and trapping it with the trapping agent of choice.

Scheme 2.17 One-Pot Generation and Trapping of Trifluoromethylphosphinidene Tungsten(0) Complex

When the reaction with DMAD was repeated in the presence of diphenylacetylene, the expected phosphirene complex was formed in 52% yield.

Though the magnitude of the one-bond phosphorus-tungsten coupling constant could not be determined, the presence of the pentacarbonyltungsten(o) group could be observed in the ^{13}C NMR spectrum, and it was confirmed crystallographically. Its molecular structure can be seen below in Figure 2.4.

Figure 2.4 X-ray Crystal Structure of 1-Trifluoromethylphosphirene Tungsten(0) Complex **19**. Main Distances (Å) and Angles (°): P1-W1: 2.4632(6), P1-C6 1.887(3), P1-C7 1.786(2), P1-C8 1.785(2); C7-P1-C8 43.50(11)

The molecular structure of the ring is extremely similar to that of 1,2,3-triphenylphosphirene pentacarbonyltungsten(o).¹² The only significant difference between the two structures lies in the phosphorus-tungsten bond length; 2.4632(11) Å in **19** compared to 2.496(1) Å for the phenyl variant.

It is logical to assume that the phosphirene complex was a result of a [2+1] cycloaddition between terminal phosphinidene complex **11** and diphenylacetylene. Terminal phosphinidene complex **11**, in turn, must have

been formed from the decomposition of the unstable 7-trifluoromethyl-7-phosphanorbornadiene complex **12**. Further evidence for this pathway was the identification of phthalate **20** as a by-product.

Scheme 2.18 Synthesis and Decomposition of 7-Trifluoromethyl-7-phosphanorbornadiene Tungsten(0) Complex

In an attempt to isolate complex **12**, phosphole complex **13** was heated in neat DMAD at 45 °C for 72 hours. The reaction was extremely sluggish, with only about 20% conversion being observed. Although noticeable decomposition had taken place, a low-field signal at +213.7 ppm, $^2J_{\text{P-F}} = 46.7$ Hz was observed and can be assigned to the 7-phosphanorbornadiene complex. Further heating leads to excessive decomposition.

The reaction was repeated with 3-hexyne as a trapping agent. The corresponding phosphirene complex **21** was obtained and isolated as a colourless oil in 69% yield.

Scheme 2.19 One-Pot Generation and Trapping of Trifluoromethylphosphinidene Tungsten(0) Complex With 3-Hexyne

With the phosphorus-tungsten coupling being observed clearly in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, we decided to compare our result with that of 1-phenyl-2,3-diethylphosphirene pentacarbonyltungsten(o).¹² **21** shows a deshielding of around 10 ppm and a stronger phosphorus-tungsten coupling constant of 280 Hz *vs.* 266 Hz. The larger coupling constant implies that **21** is a stronger acceptor than its phenyl analogue.¹³

With the successful trapping with alkynes, we turned our attention towards trapping with alkenes. The same reaction conditions were applied, except with cyclohexene as a trapping agent, and phosphirane tungsten(o) complex **22** was formed as a single isomer. This is in contrast to what is observed with aryl and alkyl substituents where an inseparable mixture of diastereomers are formed.¹⁴

Scheme 2.20 One-Pot Generation and Trapping of Trifluoromethylphosphinidene Tungsten(0) Complex With Cyclohexene

Similar to what Mathey and co-workers found with the generation and trapping of chlorophosphinidene pentacarbonyltungsten(0), with the complexing group being projected over the cyclohexyl ring.⁷ The stereochemistry was verified by X-ray crystallographic analysis and it can be seen below in Figure 2.5.

Figure 2.5 X-ray Crystal Structure of 1-Trifluoromethylphosphirane Tungsten(0) Complex **22**. Main Distances (Å) and Angles (°): P1-W1 2.4727(10), P1-C6 1.871(4), P1-C7 1.837(4), P1-C8 1.831(4), C7-C8 1.532(5); C7-P1-C8 49.37(18)

The phosphorus-tungsten bond length is long (2.4727(10) Å) and this prevents any repulsion caused by the close proximity of the cyclohexyl ring and the pentacarbonyltungsten(o) complexing group. In addition, the large phosphorus-tungsten coupling constant indicates that phosphirane tungsten(o) complex **22** is a strong acceptor.

The reaction did not work as well with electron deficient alkenes. The reaction with *trans*-stilbene was sluggish and was stopped after 72 hours. There was a signal at -163.15 ppm, $^2J_{P-F} = 46.7$ Hz. However, we were unable to isolate the product by column chromatography over silica at -10 °C. It appears that a three-membered ring is present in light of the high field chemical shift.¹⁵ Comparing the ^{31}P chemical shift against that of 1,2,3-triphenylphosphirene pentacarbonyltungsten(o) ($\delta = -120.5$ ppm), the signal is in fact, the free phosphirane **23**. No tungsten satellites were observed in the crude NMR.

Scheme 2.21 Attempted Trapping of Trifluoromethylphosphinidene Tungsten(0) Complex by *trans*-Stilbene

The extremely weak phosphorus-tungsten bond can be explained by the fact that the strongly electron withdrawing trifluoromethyl group almost suppresses backbonding from phosphorus to tungsten.

The sluggish reaction between **11** and *trans*-stilbene also sheds light on the attraction between alkenes and terminal phosphinidene complexes. It is

known that phenylphosphinidene pentacarbonyltungsten(o) forms extremely stable phosphirane complexes with *trans*-stilbene¹⁴ (decomposes at around 150 °C)¹⁶ whereas the analogous trifluoromethylphosphirane pentacarbonyltungsten(o) complex is extremely unstable. It can be explained from the strength of backbonding from the HOMO of phosphorus to the π^* orbitals (LUMO) of the alkene.

Figure 2.6 Frontier Orbital Description of Bonding Between Terminal Phosphinidene Complexes and Alkenes

With the increased electrophilicity of terminal phosphinidene complex **11**, we were tempted to check if insertions into carbon-hydrogen bonds were possible. Using the established reaction conditions and ferrocene as a trapping agent, we attempted the insertion into a carbon-hydrogen bond of ferrocene. Unfortunately, the reaction did not proceed as hoped and only a decomposition of phosphole complex **13** was observed.

Scheme 2.22 Attempted Insertion of Trifluoromethylphosphinidene Tungsten(0) Complex Into C-H Bond of Ferrocene

2.3 Conclusion

Summing up, it seems that despite the promising computational studies suggesting the heightened electrophilicity of terminal phosphinidene complex **11**, its chemistry and reactivity is closely paralleled to standard phosphinidene species. The key difference is that reactions appear to not function well with electron poor alkenes. The suppression of backbonding from phosphorus' HOMO to the alkene's LUMO is a result of the low energy of the HOMO, preventing its donation. This point highlights the importance of backbonding in stability of phosphirane complexes.

2.4 Experimental Details

2.4.1 General Considerations

All reactions with air- or moisture-sensitive manipulations were carried out under positive pressure of nitrogen using standard Schlenk techniques. Tetrahydrofuran was distilled from sodium-benzophenone, toluene was distilled from sodium, dichloromethane was distilled from phosphorus pentoxide and hexane was distilled from sodium. All other solvents were used as received. Column chromatography was performed on silica gel (40-63 microns). NMR spectra were recorded on a Bruker Avance 500 spectrometer (500 MHz for ^1H , 125 MHz for ^{13}C , 202 MHz for ^{31}P), or Bruker Avance III 400 spectrometer (400 MHz for ^1H , 100 MHz for ^{13}C , 162 MHz for ^{31}P , 376 MHz for ^{19}F). Chemical shifts are reported in δ (ppm), referenced to the residual solvent resonance of d_2 -dichloromethane for ^1H NMR ($\delta = 5.32$) and ^{13}C NMR ($\delta = 53.84$). ^{31}P chemical shifts are referenced to an external standard of 85% H_3PO_4 in H_2O ($\delta = 0.00$) and are uncorrected. Multiplicities are given as: s (singlet), d (doublet), dd (doublet of doublets), t

(triplet), q (quartet), m (multiplet). The number of protons (n) for a given resonance are given by nH and coupling constants are given as a J value in Hz. Mass spectra were recorded on a JEOL AccuTOF-DART HRMS. Elemental analyses were performed using Euro Vector Euro EA Elemental Analyser (CHNS).

2.4.2 Experimental Procedures

17

3,4-Dimethyl-1-phenylphosphole (**17**)

To a large, ice-cooled, nitrogen-flushed flask was added phenyldibromophosphane (54 mL), phenyldichlorophosphane (51 mL), 2,3-dimethyl-1,3-butadiene (89 mL) and dichloromethane (40 mL). The flask was flushed with nitrogen, capped, sealed and mixed vigorously. It was left standing at 0 °C for 4 hours followed by standing at room temperature in the dark for 21 days.

The flask was cooled to 0 °C and in succession, hexane (150 mL), dichloromethane (100 mL), 2-picoline (160 mL) was added. The flask was flushed with nitrogen, capped, sealed and stirred in an ice bath overnight. Thereafter, the flask was cooled to 0 °C and 3M hydrochloric acid (150 mL) was added. The mixture was transferred to a large separatory funnel. The organic layer was removed and the aqueous layer was extracted with hexane (3 x 80 mL). The combined organic extracts were washed with water (100

mL) until the aqueous layer was neutral. The organic extracts were filtered over magnesium sulfate and evaporated to dryness.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2): δ 1.78 (s); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2): δ 18.00 (d, $^3J_{\text{P-C}} = 4.0$ Hz, 2C, $-\text{CH}_3$), 128.82 (d, $^1J_{\text{P-C}} = 8.0$ Hz, 2C, $-\text{PCH}$), 129.19 (s, 1C, *para-C*), 130.17 (d, $^3J_{\text{P-C}} = 2.0$ Hz, 2C, *meta-C*), 132.90 (d, $^1J_{\text{P-C}} = 12.0$ Hz, 1C, *ipso-C*), 133.61 (d, $^2J_{\text{P-C}} = 18.0$ Hz, 2C, *ortho-C*), 149.44 (d, $^2J_{\text{P-C}} = 9.0$ Hz, 2C, $-\text{CCH}_3$); ^1H NMR (400 MHz, CD_2Cl_2): δ 2.30 (d, $^4J_{\text{P-H}} = 3.2$ Hz, 6H, $-\text{CH}_3$), 6.69 (d, $^2J_{\text{P-H}} = 38.8$ Hz, 2H, $-\text{PCH}$), 7.41-7.43 (m, 3H, *Ar-H*), 7.52-7.56 (m, 2H, *Ar-H*)

18

Lithium 3,4-dimethylphospholide (**18**)

Under an inert atmosphere of nitrogen, to a solution of **17** (2 mL, 11.0 mmol) in THF (20 mL) was added lithium (in excess) and stirred at room temperature for 5.5 hours. The lithium was removed, *t*-BuCl (2.4 mL, 22.0 mmol) added and warmed to 65 °C for 1.5 hours.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, THF): δ 57.40 (s)

15

Lithium 3,4-dimethylphospholide pentacarbonyltungsten(o) (**15**)

To the solution of **18** was added tungsten(o) hexacarbonyl (3.87 g, 11 mmol) and stirred at room temperature for 14 hours under an inert atmosphere of nitrogen.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, THF): δ -54.74 (s, $^1\text{J}_{\text{P-W}} = 104$ Hz)

13

3,4-Dimethyl-1-(trifluoromethyl)phosphole pentacarbonyltungsten(o) (**13**)

Under an inert atmosphere of nitrogen, the solution of **15** was cooled to 0 °C in an ice-bath and 1-(trifluoromethyl)-1,2-benziodoxol-3-(1H)-one (4.17 g, 13.2 mmol) was added portionwise and stirred for 1 h. The crude product was purified directly by flash column chromatography over silica at -10 °C with hexanes, yielding the target phosphole complex as a pale yellow solid (1.164 g, 21% yield).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2): δ 27.16 (q, $^2\text{J}_{\text{P-F}} = 70.2$ Hz, $^1\text{J}_{\text{P-W}} = 235$ Hz);

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CD_2Cl_2): δ - 60.49 (d, $^2\text{J}_{\text{P-F}} = 70.7$ Hz); $^{13}\text{C}\{^1\text{H}\}$

NMR (125 MHz, CD_2Cl_2): δ 17.85 (d, $^3\text{J}_{\text{P-C}} = 11.7$ Hz, 2C, -CH₃), 121.59 (d, $^1\text{J}_{\text{P-C}} = 42.3$ Hz, 2C, -PCH), 127.64 (qd, $^1\text{J}_{\text{C-F}} = 317.8$ Hz, $^1\text{J}_{\text{P-C}} = 52.6$ Hz, 1C, -CF₃),

158.42 (d, $^2J_{P-C} = 8.4$ Hz, 2C, -CCH₃), 194.57 (d, $^2J_{P-C} = 6.5$ Hz, 4C, *cis*-CO), 197.81 (d, $^2J_{P-C} = 23.0$ Hz, 1C, *trans*-CO); 1H NMR (500 MHz, CD₂Cl₂): δ 2.22 (s, 6H, -CH₃), 6.27 (dd, $^2J_{P-H} = 38.8$ Hz, $^4J_{H-H} = 0.7$ Hz, 2H, PCH)

HRMS m/z : 503.9573 (calcd. for C₁₂H₈F₃O₅P¹⁸⁴W: 503.9571)

Anal. calcd. for C₁₂H₈F₃O₅PW: C 28.60, H 1.60 Found: C 29.388, H 1.629.

19

2,3-Diphenyl-1-(trifluoromethyl)phosphirene pentacarbonyltungsten(o)
(**19**)

A Schlenk tube was charged with **13** (75.6 mg, 0.15 mmol), dimethyl acetylenedicarboxylate (0.5 mL, 4.0 mmol) and diphenylacetylene (142.6 mg, 0.8 mmol) and toluene (0.5 mL) and heated at 80 °C for 48 h. The crude product was purified directly by flash column chromatography over silica at -10 °C with hexanes, yielding the target phosphirene complex as a pale yellow solid (46.3 mg, 52% yield).

$^{31}P\{^1H\}$ NMR (202 MHz, CD₂Cl₂): δ -153.83 (q, $^2J_{P-F} = 69.9$ Hz); $^{19}F\{^1H\}$ NMR (376 MHz, CD₂Cl₂): δ -62.29 (d, $^2J_{P-F} = 69.5$ Hz); $^{13}C\{^1H\}$ NMR (125 MHz, CD₂Cl₂): δ 125.19 (d, $^1J_{P-C} = 13.8$ Hz, 2C, P-C=C), 126.12 (d, $^2J_{P-C} = 6.1$ Hz, 2C, *ipso*-C), 129.98 (s, 4C, *meta*-C), 131.10 (d, $^3J_{P-C} = 6.0$ Hz, 4C, *ortho*-C), 132.14 (s, 2C, *para*-C), 194.39 (d, $^2J_{P-C} = 8.4$ Hz, 4C, *cis*-CO), 196.51 (d, $^2J_{P-C} = 37.6$ Hz, 1C, *trans*-CO); 1H NMR (500 MHz, CD₂Cl₂): δ 7.57 – 7.68 (m, 6H, Ar-*H*), 7.89 – 7.98 (m, 4H, Ar-*H*)

HRMS m/z : 601.9731 (calcd. for $C_{20}H_{10}F_3O_5P^{184}W$: 601.9727)

Anal. calcd. for $C_{20}H_{10}F_3O_5PW$: C 39.90, H 1.67. Found: C 40.981, H 2.044.

20

Dimethyl-4,5-dimethylphthalate (**20**)

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 19.65 (s, 2C, Ar- CH_3), 52.45 (s, 2C, $COOCH_3$), 129.38 (s, 2C, C- CH_3), 130.04 (s, 2C, C-H), 140.23 (s, 2C, C- $COOCH_3$), 168.28 (s, 2C, $COOCH_3$); 1H NMR (500 MHz, $CDCl_3$): δ 2.31 (s, 6H, C- CH_3), 3.88 (s, 6H, $COOCH_3$), 7.49 (s, 2H, Ar-H)

21

2,3-Diethyl-1-(trifluoromethyl)phosphirene pentacarbonyltungsten(o) (**21**)

A Schlenk tube was charged with **13** (75.6 mg, 0.15 mmol), dimethyl acetylenedicarboxylate (0.5 mL, 4.0 mmol) and hex-3-yne (186.2 μ L, 1.6 mmol) and toluene (0.5 mL) and heated at 80 $^{\circ}C$ for 48 h. The crude product was purified directly by flash column chromatography over silica at -10 $^{\circ}C$ with hexanes, yielding the target phosphirene complex as a colourless oil (52 mg, 69% yield).

$^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2): δ -152.58 (q, $^2J_{P-F}$ = 67.1 Hz, $^1J_{P-W}$ = 280 Hz); $^{19}F\{^1H\}$ NMR (376 MHz, CD_2Cl_2): δ -63.22 (d, $^2J_{P-F}$ = 66.7 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 12.03 (d, $^3J_{P-C}$ = 4.5 Hz, 2C, - CH_2CH_3), 19.94 (d,

$^2\text{J}_{\text{P-C}} = 5.9$ Hz, 4C, $-\text{CH}_2\text{CH}_3$), 125.94 (poorly resolved, $^1\text{J}_{\text{C-F}} = 321.9$ Hz, $^1\text{J}_{\text{P-C}} = 4.3$ Hz, 1C, $-\text{CF}_3$), 130.17 (d, $^1\text{J}_{\text{P-C}} = 16.8$ Hz, 2C, $\text{P-C}=\text{C}$), 194.85 (d, $^2\text{J}_{\text{P-C}} = 8.5$ Hz, 4C, *cis*-CO), 197.20 (d, $^2\text{J}_{\text{P-C}} = 36.6$ Hz, 1C, *trans*-CO); ^1H NMR (500 MHz, CD_2Cl_2): δ 1.31 (t, $^3\text{J}_{\text{H-H}} = 7.5$ Hz, 6H, $-\text{CH}_2\text{CH}_3$), 2.76 (m, 4C, $-\text{CH}_2\text{CH}_3$)
 HRMS m/z : 505.9730 (calcd. for $\text{C}_{12}\text{H}_{10}\text{F}_3\text{O}_5\text{P}^{184}\text{W}$: 505.9727)

Anal. calcd. for $\text{C}_{12}\text{H}_{10}\text{F}_3\text{O}_5\text{PW}$: C 28.48, H 1.99. Found: C 29.042, H 1.753.

22

7-(Trifluoromethyl)-7-phosphabicyclo[4,1,0]heptane
 pentacarbonyltungsten(o) (**22**)

A Schlenk tube was charged with **13** (75.6 mg, 0.15 mmol), dimethyl acetylenedicarboxylate (0.5 mL, 4.0 mmol) and cyclohexene (0.5 mL, 4.9 mmol) and toluene (0.5 mL) and heated at 80 °C for 48 h. The crude product was purified directly by flash column chromatography over silica at -10 °C with hexanes, yielding the target phosphirane complex as a white solid (56.4 mg, 75% yield).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2): δ -143.66 (q, $^2\text{J}_{\text{P-F}} = 67.2$ Hz, $^1\text{J}_{\text{P-W}} = 272$ Hz); $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CD_2Cl_2): δ -58.95 (d, $^2\text{J}_{\text{P-F}} = 67.0$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2): δ 20.51 (d, $^1\text{J}_{\text{P-C}} = 17.6$ Hz, 2C, CH), 21.49 (d, $^3\text{J}_{\text{P-C}} = 2.5$ Hz, 4C, $-\text{CH}_2-$), 21.57 (d, $^2\text{J}_{\text{P-C}} = 3.0$ Hz, 4C, $-\text{CH}_2-$), 127.93 (poorly resolved, $^1\text{J}_{\text{C-F}} = 315.1$ Hz, $^1\text{J}_{\text{P-C}} = 35.3$ Hz, 1C, $-\text{CF}_3$), 194.46 (d, $^2\text{J}_{\text{P-C}} = 8.0$ Hz, 4C, *cis*-CO), 196.20 (d, $^2\text{J}_{\text{P-C}} = 37.8$ Hz, 1C, *trans*-CO); ^1H NMR (500 MHz,

CD_2Cl_2): δ 1.39-1.51 (m, 4H, alkyl-H), 1.81-1.89 (m, 2H, alkyl-H), 2.28-2.37 (m, 4H, alkyl-H)

HRMS m/z : 505.9730 (calcd. for $\text{C}_{12}\text{H}_{10}\text{F}_3\text{O}_5\text{P}^{184}\text{W}$: 505.9727)

Anal. calcd. for $\text{C}_{12}\text{H}_{10}\text{F}_3\text{O}_5\text{PW}$: C 28.48, H 1.99. Found: C 29.604, H 1.957.

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3

New Precursors To Terminal Phosphinidene Complexes

The [4+2] cycloaddition of phosphole tungsten(o) complexes with *p*-benzoquinone yields the corresponding 7-phosphanorbornene complexes. Upon treatment with a bulky base, and subsequent quenching of the phenoxide anions, benzo-7-phosphanorbornadiene complexes are generated. These complexes are precursors to terminal phosphinidene complexes. Preliminary results show that phosphinidene tetracarbonyliron(o) complexes can be generated by the [4+2] cycloaddition between phosphole iron(o) complexes and *p*-benzoquinone, followed by oxidation by excess *p*-benzoquinone.

3.1 Introduction

Terminal phosphinidene complexes have been generated by a number of ways. Of these methods, the 7-phosphanorbornadiene complex, first reported by Mathey and co-workers in 1982,¹ has been utilised to the largest extent in light of their wide substrate scope and easy syntheses.

Scheme 3.1 Cheletropic Elimination of Terminal Phosphinidene Complexes From 7-Phosphanorbornadiene Complexes

The decomposition of these strained compounds is driven by the formation of an aromatic phthalate **20**. The syntheses of 7-phosphanorbornadiene complexes are easily performed by the [4+2] cycloaddition between phosphole complexes and DMAD.

Scheme 3.2 Synthesis of 7-Phosphanorbornadiene Complexes

The fact that an aromatic moiety such as phthalate **20** needs to be formed necessitates the utilization of alkynes as dienophiles. The alkyne also needs to be activated by two electron withdrawing groups, drastically decreasing the electron density around the carbon-carbon triple bond. Another point to note is that the temperature of the cycloaddition is close to the temperature required for decomposition. This means that if more forcing conditions are required, this route may not be feasible.

While this route appears to have a large functional group tolerance, it is not without its drawbacks. Large groups such as *tert*butyl are not tolerated. The reason is fairly straightforward; the [4+2] cycloadditions between phosphole complexes and DMAD usually takes place on the opposite side of the metal centre, suggesting that the reaction is fairly sensitive to steric hindrance. The *tert*butyl group is large and poses a sizable impediment to the cycloaddition.

Another class of phosphinidene complexes that cannot be generated with the 7-phosphanorbornadiene framework are the aminophosphinidenes. The

phosphorus-nitrogen bond is weak and adds across the carbon-carbon triple bond of DMAD.

Scheme 3.3 Addition of P-N Across C-C Triple Bond of DMAD

With these imposed limitations, we were looking for other systems for the generation of terminal phosphinidene complexes. In this chapter, we highlight our progress in the synthesis of 7-phosphanorbornadiene complexes from 7-phosphanorbornene complexes derived from *p*-benzoquinone.

3.2 Results and Discussion

The synthesis of phenylphosphole tungsten(o) complexes from phenylphosphole was done by creating a vacancy on the tungsten atom, allowing for coordination of the phosphole lone pair to the tungsten(o) metal centre. This was achieved by reacting tungsten(o) hexacarbonyl with trimethylamine-N-oxide.

Scheme 3.4 Creation of Vacant Site on Tungsten(0)

The metal complex was not purified and 3,4-dimethyl-1-phenylphosphole **17** was added directly and stirred overnight, to yield phosphole complex **24**.²

Scheme 3.5 Coordination of 1-Phenylphosphole To Tungsten(0) Centre

Phosphole complex **24** was reacted with *p*-benzoquinone at 80 °C. Monitoring the reaction by $^{31}\text{P}\{^1\text{H}\}$ NMR revealed the complete disappearance of the starting material in 60 hours with the appearance of a signal at +52 ppm.

Scheme 3.6 Cycloaddition of 1-Phenylphosphole Tungsten(0) Complex With *p*-Benzoquinone

The molecular structure of 7-phenyl-7-phosphanorbornene tungsten(o) complex **25** was confirmed by X-ray crystallographic analysis.

Figure 3.1 X-ray Crystal Structure of 7-Phenyl-7-Phosphanorbornene Tungsten(0) Complex **25**. Main Distances (Å) and Angles (°): P1-W1 2.4970(6), P1-C8 1.8596(16), C8-C11 1.559(2), C11-C12 1.513(2), C12-O4 1.212(2), C12-C13 1.464(3), C13-C13A 1.330(4) C11-C11A 1.555(3); C8-P1-C8A 80.60(10)

As expected, the cycloaddition took place on the side opposite the sterically imposing pentacarbonyltungsten(o) complexing group. Also similarly expected was the endo stereochemistry at the ring junction.

The two protons at the ring junctions are α to carbonyl groups. We envisaged that their lower pKa would allow for them to be removed with mild bases. We first experimented with sodium methoxide.

Scheme 3.7 Base-Catalyzed Decomposition of 7-Phenyl-7-Phosphanorbornene Tungsten(0) Complexes

Phosphinite complex **26** represents the formal insertion of phenylphosphinidene pentacarbonyltungsten(o) into the oxygen-hydrogen bond of methanol. The low-field chemical shift (+108 ppm) and large phosphorus-tungsten coupling constant (276 Hz) implies the presence of an electron withdrawing group directly attached to the phosphorus atom. The large phosphorus-hydrogen coupling constant (347 Hz) is consistent with a one-bond coupling between the two NMR active nuclei.³

The formation of phosphinite complex **26** is probably the result of nucleophilic attack of the methoxide anion on the phosphorus bridge, causing it to collapse due to quarterization of the phosphorus bridgehead.⁴ This product has been isolated and fully characterised previously.⁵

It was obvious that the solution to this was to utilize a base that was basic, but not nucleophilic. Lithium diisopropylamine (LDA) was a candidate that fit the requirements, with the two isopropyl moieties interfering with the large tungsten complexing group.

The reaction was repeated with the dropwise addition of LDA to a THF solution of 7-phenyl-7-phosphanorbornene complex **25**. Upon addition of

LDA, the solution darkened and slowly turned dark green. A $^{31}\text{P}\{^1\text{H}\}$ NMR was acquired but no signal could be detected. However, the appearance of the spectrum suggested the presence of a paramagnetic species interfering with the acquisition. The solution was filtered over celite and a $^{31}\text{P}\{^1\text{H}\}$ NMR was acquired. A new signal at +169 ppm was observed. Purification by column chromatography yielded benzo-7-phenyl-7-phosphanorbornadiene complex **27**. The ^1H NMR revealed a broad singlet at 4.57 ppm with an integration ratio of 2, consistent with the biphenol structure proposed.

Scheme 3.8 Aromatization of 7-Phenyl-7-Phosphanorbornene Complexes After Treatment With LDA

A single crystal suitable for X-ray analysis was grown from DCM/DEE at room temperature and the molecular structure of **27** was confirmed.

Figure 3.2 X-ray Crystal Structure of Benzo-7-Phenyl-7-Phosphanorbornadiene Tungsten(0) Complex **27**. Main Distances (Å) and Angles (°): P1-W1 2.490(3), P1-C12 1.887(11), P1-C17 1.870(11), C18-C19 1.409(14), C19-C20 1.378(14), C20-C21 1.392(13), C21-C22 1.383(14), C22-C23 1.375(14) C23-C18 1.369(14), C20-O6 1.389(11), C23-O7 1.373(11); C12-P1-C17 79.9(5)

Analysis of the X-ray structure shows the carbon-carbon bond lengths of the C18-C23 ring to be fairly similar, ranging from 1.369(14) Å to 1.392(13) Å, with the exception of C18-C19 (1.409(14) Å), suggesting aromatization of the ring.

Formation of benzo-7-phenyl-7-phosphanorbornadiene complex **27** is probably from deprotonation of both α -protons of 7-phenyl-7-phosphanorbornene complex **25**, followed from protonation at the oxygen atoms from adventitious moisture.

As it is known that oxygen-hydrogen bonds interfere with the generation and subsequent trapping of terminal phosphinidene complexes,⁵⁻⁶ we decided to alkylate the dianion.

Alkylation with methyl iodide proved to be inefficient; a crude $^{31}\text{P}\{^1\text{H}\}$ showed a mixture of products being formed. The mixture primarily comprised of alkylated and protonated dianions.

Scheme 3.9 Attempted Alkylation of Diphenoxide Anion With Methyl Iodide

A stronger methyl electrophile was required. Methyl triflate was found to be an effective methylating agent, effectively suppressing protonation, and the dialkylated product was formed predominantly in 43% yield.

Scheme 3.10 Alkylation of Diphenoxide Anion With Methyl Triflate

The molecular structure of **28** was confirmed by X-ray crystallography.

Figure 3.3 X-ray Crystal Structure of Benzo-7-Phenyl-7-Phosphanorbornadiene Tungsten(0) Complex **28**. Main Distances (Å) and Angles (°): P1-W1 2.491(2), P1-C6 1.848(9), P1-C11 1.874(9), C12-C19 1.380(12), C12-C13 1.407(11), C13-C15 1.381(12), C15-C16 1.388(13), C16-C17 1.370(11), C17-C19 1.385(11), C13-O6 1.376(10), C17-O7 1.361(10); C6-P1-C11 80.8(4)

With a potential precursor of terminal phosphinidene complexes, we subjected **28** to conditions similar to those required to decompose 7-phosphanorbornadiene complexes derived from DMAD. Heating **28** at 110

°C in toluene for 16 hours with diphenylacetylene as a trapping agent showed almost no decomposition.

The reaction was repeated at 140 °C in xylene for 16 hours. $^{31}\text{P}\{^1\text{H}\}$ NMR of the crude mixture revealed the conversion to be around 20%.

Scheme 3.11 Attempted Thermal Decomposition of Benzo-7-Phenyl-7-Phosphanorbornadiene Tungsten(0) Complex

The harsh conditions required to force cheletropic elimination of the phosphorus bridgehead led us to the use of copper(I) chloride as a catalyst.⁷ In toluene at 70 °C with the addition of copper(I) chloride, the reaction took two hours for completion, yielding the triphenylphosphirene complex in 25% yield.

Scheme 3.12 CuCl-Catalysed Decomposition of Benzo-7-Phenyl-7-Phosphanorbornadiene Tungsten(0) Complex and Subsequent Trapping With Diphenylacetylene

The cheletropic elimination took place with the formation of aromatic naphthalene derivative **30** as a driving force. The molecular structure of **30** has also been confirmed crystallographically.

Figure 3.4 X-ray Crystal Structure of Naphthalene Derivative **30**

Under the same reaction conditions, *trans*-stilbene was also used as a trapping agent, forming the expected phosphirane tungsten(o) complex in 55% yield.

Scheme 3.13 CuCl-Catalysed Decomposition of Benzo-7-Phenyl-7-Phosphanorbornadiene Tungsten(0) Complex and Subsequent Trapping With Diphenylacetylene

With 2,3-dimethylbutadiene as a trapping agent, the temperature was raised to $110\text{ }^\circ\text{C}$ to enable conversion of the initial diastereomeric adducts, 2-vinylphosphirane tungsten(o) complexes, into the corresponding 3-phospholene tungsten(o) complex.^{7a}

Scheme 3.14 Trapping of Terminal Phosphinidene Complex With 2,3-Dimethylbutadiene and Its Isomerization Into 1-Phenylphosphol-3-ene Tungsten(0) Complex

In order to check the generality of the reaction, we tried the reaction with the methyl analogue. The methylphosphole complex **33** was synthesized from methylation of **15** with methyl iodide.⁸

Scheme 3.15 Synthesis of 1-Methylphosphole Tungsten(0) Complex

Subjecting methylphosphole complex **33** to the same experimental conditions yielded the corresponding 7-methyl-7-phosphanorbornene complex **34**.

Scheme 3.16 [4+2] Cycloaddition of 1-Methylphosphole Tungsten(0) Complex and *p*-Benzoquinone

Treatment of **34** with LDA followed by methyl triflate gave benzo-7-methyl-7-phosphanorbornadiene complex **35**.

Scheme 3.17 Treatment of 7-Methyl-7-Phosphanorbornene Tungsten(0) Complex With LDA, Followed By Methylation

The molecular structure of **35** was also confirmed by single crystal X-ray crystallography.

Figure 3.5 X-ray Crystal Structure of Benzo-7-Methyl-7-Phosphanorbornene Tungsten(0) Complex **35**. Main Distances (Å) and Angles (°): P1-W1 2.508(2), P1-C5 1.881(6), C8-C8A 1.386(11), C8-C9 1.394(8), C9-C10 1.396(8), C10-C10A 1.388(12), C9-O4 1.384(7); C5-P1-C5A 79.7(4)

Unfortunately, **35** proved to be a poor precursor to terminal phosphinidene complexes. Heating a toluene solution of **35**, copper(I) chloride and diphenylacetylene to 70 °C for 5 hours led to extremely low conversion. A signal at around -169 ppm was observed which corresponds to the expected methylphosphirene complex **36**.

Scheme 3.18 Attempted Decomposition of Benzo-7-Methyl-7-Phosphanorbornadiene Tungsten(0) Complex and Subsequent Trapping With Diphenylacetylene

It is not known definitively why these benzoannelated compounds show such a high stability. A comparison of the X-ray structures of **28** and 7-phenyl-7-phosphanorbornadiene pentacarbonyltungsten(0) **37** (generated from the [4+2] cycloaddition between 1-phenylphosphole tungsten(0) complex **24** and DMAD) show that the phosphorus-carbon bond lengths at the bridgehead have fairly similar average lengths (1.861 Å in **28** vs. 1.875 Å in **37**) and bond angles (80.8° in **28** vs. 79.4° in **37**). One possible reason could be the additional stability induced by benzoannelation.⁹ Lammertsma and co-workers have calculated that for the phosphepine framework, benzoannelation has a stabilizing effect of about 15.2 kcal mol⁻¹.¹⁰ The substantial stabilization could be responsible for the sluggish decomposition of this class of compounds.

Figure 3.6 X-ray Crystal Structure of 7-Phenyl-7-Phosphanorbornadiene Tungsten(0) Complex **37**. Main Distances (Å) and Angles (°): P1-W1 2.4809(6), P1-C6 1.874(3), P1-C9 1.875(2), C10-C11 1.341(3); C6-P1-C9 79.42(11)

Nevertheless, with a protocol for the synthesis of 7-phosphanorbornadiene complexes, we decided to attempt the synthesis of 7-phosphanorbornadiene complexes in the hope of generating phosphinidenes that cannot be made generated from 7-phosphanorbornadienes stemming from a synthesis involving DMAD as a dienophile. Our first target was the aminophosphinidene complex.

Previous syntheses of aminophosphinidene complexes necessitated the use of 1-aminophosphirane complexes as a generating system. The syntheses of these complexes are tedious multistep processes involving either the insertion of β -chloroethylphosphinidene complex into a nitrogen-hydrogen bond of an amine, followed by cyclization or from the reaction of primary phosphines with *n*-butyllithium followed by quenching of the anion with 1,2-dichloroethane.

Scheme 3.19 Current Synthetic Routes To 1-Aminophosphirane Tungsten(0) Complexes

In a bid to reduce the electron density of the nitrogen atom, we used diphenylamine as a substituent. We hoped that *p*-benzoquinone would be a poorer electrophile than DMAD, allowing the [4+2] cycloaddition to take place, yielding benzo-7-diphenylamino-7-phosphanorbornadiene tungsten(0) complex **38** after metalation and methylation, eventually generating a phosphinidene complex **39** that could be trapped with diphenylacetylene, forming phosphirene complex **40**. The proposed synthetic route can be seen in Scheme 3.20.

Scheme 3.20 Potential Generation of Diphenylaminophosphinidene Tungsten(0) Complex

Synthesis of diphenylaminophosphole complex **41** was achieved by treating cyanophosphole complex **14** with lithium diphenylamide.

Scheme 3.21 Synthesis of 1-(Diphenylamino)phosphole Tungsten(0) Complex

Phosphole complex **41** was reacted with *p*-benzoquinone, giving the corresponding 7-amino-7-phosphanorbornene complex **42**.

Scheme 3.22 [4+2] Cycloaddition Between 1-(Diphenylamino)phosphole Tungsten(0) Complex and *p*-Benzoquinone

Unfortunately, when **42** was treated with LDA, followed with methyl triflate, only decomposition was observed.

Scheme 3.23 Attempted Metalation of 7-(Diphenylamino)-7-Phosphanorbornene Tungsten(0) Complex

We turned our attention to the potential generation of *tert*butylphosphinidene tungsten(o) complex. In this aspect, we were met

with even more limited success as compared to the attempted synthesis of 7-amino-7-phosphanorbornadiene tungsten(o) complex. We were unable to force the cycloaddition to take place to any appreciable extent. When reacted with *p*-benzoquinone under the established reaction conditions, a small signal was observed at +68.85 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, which we assign to 7-*tert*butyl-7-phosphanorbornene tungsten(o) complex **44** on the basis of its chemical shift. However, efforts to activate the system with Lewis acids or by using more forcing conditions only led to decomposition.

Scheme 3.24 Attempted Synthesis of 7-*Tert*butyl-7-Phosphanorbornene Tungsten(0) Complex

With these setbacks, we decided to look at whether this method could be used for modification of the group used to protect the phosphorus lone pair. One obvious choice would be to try phosphorus sulfides. It has been reported that 7-phenyl-7-phosphanorbornadiene sulfides made from 3,4-dimethyl-1-phenylphosphole sulfide **45** and DMAD are unstable and breakdown at room temperature, yielding a phosphinidene sulfide.¹¹

Scheme 3.25 Rapid Decomposition of 7-Phenyl-7-Phosphanorbornadiene Sulfide Into Phenylphosphinidene Sulfide

We hoped that with this current protocol, benzoannulation would provide some stabilization, allowing for a bench-stable precursor to phosphinidene sulfides that does not require harsh conditions for generation.¹²

Reacting phosphole sulfide **45** with *p*-benzoquinone at 80 °C yielded the 7-phenyl-7-phosphanorbornene sulfide **46**.

Scheme 3.26 Synthesis of 7-Phenyl-7-Phosphabornene Sulfide

Analysis of the X-ray crystal structure revealed that the cycloaddition takes place on the opposite side of the substituent, contrary to what is observed when a metal complexing group is utilised. This is expected when comparing the size of the sulfur atom when compared to the phenyl group.

Figure 3.7 X-ray Crystal Structure of 7-Phenyl-7-Phosphanorbornene Sulfide **46**. Main Distances (Å) and Angles (°): P1-S1 1.9443(7), P1-C1 1.838(2), C1-C10 1.841(2), C1-C4 1.557(3), C4-C9 1.560(3), C4-C5 1.518(3), C5-O1 1.217(3); C1-P1-C10 82.39(9)

46 was treated sequentially with LDA and methyl triflate in an attempt to generate the corresponding 7-phosphanorbornadiene sulfide. Unfortunately, only decomposition was observed, probably breaking down into the phosphinidene sulfide and naphthalene derivative **30**.

Scheme 3.27 Attempted Synthesis of Benzo-7-Phenyl-7-Phosphanorbornadiene Sulfide

We were wondering if a different metal complexing group could be utilised. We experimented with the usage of tetracarbonyliron(o) in place of pentacarbonyltungsten(o). The use of iron phosphole complexes as dienes

and DMAD as a dienophile in the synthesis of 7-phosphanorbornadienes has not been successful; loss of the phosphorus bridge was observed.¹³

The synthesis of 3,4-dimethyl-1-phenylphosphole tetracarbonyliron(0) complex **47** was performed by stirring a solution of phosphole **17** with diiron nonacarbonyl at room temperature.

Scheme 3.28 Synthesis of 1-Phenylphosphole Iron(0) Complex

The molecular structure of **47** was confirmed by X-ray crystallography.

Figure 3.8 X-ray Crystal Structure of 1-Phenylphosphole Iron(0) Complex **47**. Main Distances (Å) and Angles (°): P1-Fe1 2.2316(6), P1-C5 1.7986(18), C5-C6 1.341(3), C6-C7 1.494(3), C7-C8 1.339(3), P1-C8 1.793(2); C5-P1-C8 91.55(9)

In solid state, the phosphole moiety occupies an apical position. Analysis of the $^{13}\text{C}\{^1\text{H}\}$ NMR shows the presence of only one carbonyl environment ($\delta = +213.15$ ppm, $^1J_{\text{P-C}} = 19.0$ Hz). This disparity can be explained by isomerization of the ligands around the iron(0) centre by a mechanism such as Berry pseudorotation or turnstile rotation and that this process must take place at a rate faster than the timescale of acquisition of an NMR spectrum.¹⁴

With the 1-phenylphosphole iron(0) complex **47** in hand, we attempted the cycloaddition with *p*-benzoquinone. Unfortunately, no reaction was observed.

Scheme 3.29 Attempted Direct [4+2] Cycloaddition of 1-Phenylphosphole Iron(0) Complex and *p*-Benzoquinone

When activated by Lewis acids, the reaction appeared to progress. Indeed, an aromatic by-product was isolated when boron trifluoride was used as a catalyst.

Scheme 3.30 Lewis Acid-Catalysed [4+2] Cycloaddition of 1-Phenylphosphole Iron(0) Complex and *p*-Benzoquinone

The formation of **49** can be rationalised by a [4+2] cycloaddition, forming **48**, followed by oxidation by an excess of *p*-benzoquinone, followed by cheletropic elimination, yielding phosphinidene iron(0) complex **50**. *p*-Benzoquinone has been known to oxidatively form carbon-carbon double bonds.¹⁵

Scheme 3.31 Proposed Mechanism For Formation of Naphthoquinone Derivative **49**

In order to check this hypothesis, we decided to attempt to trap the iron phosphinidene complex *in situ* by running the reaction in the presence of a trapping agent. It soon became clear that boron trifluoride was too strong a Lewis acid, preventing the efficient generation and trapping of the iron phosphinidene complex. A screening of different Lewis acids and conditions gave anhydrous iron(II) chloride in toluene at 75 °C to be the most optimal. When run in the presence of diphenylacetylene, we were able to detect the presence of the phosphirene complex at -90.89 ppm.

Scheme 3.32 Generation and Trapping of Phenylphosphinidene Iron(0) Complex With Diphenylacetylene

Conversion of **47** to **51** was poor, and prolonged heating or increased temperatures led to rapid decomposition of **51**, highlighting the unique effect Group VI pentacarbonyls have on the stabilization of unstable frameworks.⁵ When the temperature was lowered to 60 °C, trapping of the terminal phosphinidene complex formed was inefficient, possibly due to the reduced electrophilicity of the phosphinidene iron(o) species as compared to the tungsten(o) variant.

Inspired by Streubel's synthesis of azaphosphiranes and oxaphosphiranes,¹⁶ we wondered whether building a sufficient steric bulk around the strained three-membered ring would allow for prevention of decomposition. We decided to use bis(trimethylsilyl)acetylene as a trapping agent. Disappointingly, we were not able to trap and stabilise the phosphirene complex sufficiently, though a high-field signal was detected at -135.97 ppm in the $^{31}\text{P}\{^1\text{H}\}$ spectrum, which probably corresponds to phosphirene complex **50**.

Scheme 3.33 Generation and Trapping of Phenylphosphinidene Iron(0) Complex With Bis(trimethylsilyl)acetylene

The last point that we considered was whether the stability of **28** would allow for decomplexation. The only example of a 7-phosphanorbornadiene complex that has been decomplexed was reported by Lammertsma and co-workers in 2000.¹⁷ This was possible by the addition of a tether, reducing the planarity of the aromatic system, destabilising the organic fragment.

Scheme 3.34 First Example of Decomplexation of 7-Phosphabornadiene Complexes

Employing the same system, a solution of iodine in DCM was added, but no decomplexation was observed.

Scheme 3.35 Attempted Decomplexation of Benzo-7-Phenyl-7-Phosphanorbornadiene Tungsten(0) Complex

A direct decomplexation under positive pressure of carbon monoxide gas was attempted but no decomplexation took place.

Scheme 3.36 Attempted Decomplexation Under Positive Pressure of CO

It is known that phosphine molybdenum(o) complexes are much easier to decomplex than their tungsten(o) variants due to the drastically decreased phosphorus-metal bond strength.¹⁸ To facilitate the decomplexation, the molybdenum analogue was synthesized by an analogous procedure.

Synthesis of the phosphole molybdenum(o) complex **56** was carried out by reacting 3,4-dimethyl-1-phenylphosphole with molybdenum(o) hexacarbonyl in refluxing dichloromethane.

Scheme 3.37 Synthesis of 1-Phenylphosphole Molybdenum(0) Complex

Phosphole molybdenum(o) complex **56**, when reacted under the established reaction conditions, gave 7-phenyl-7-phosphanorbornene molybdenum(o) complex **57** in 62% yield.

Scheme 3.38 [4+2] Cycloaddition of 1-Phenylphosphole Molybdenum(0) Complex and *p*-Benzoquinone

57 was treated with LDA and methyl triflate, yielding benzo-7-phenyl-7-phosphanorbornadiene molybdenum(o) complex **58**.

Scheme 3.39 Synthesis of Benzo-7-Phenyl-7-Phosphanorbornadiene Molybdenum(0) Complex

58 was dissolved in toluene and heated to 100 °C under 50 bar of carbon monoxide gas. However, no decomplexation was observed. When the reaction was repeated at 120 °C, a loss of phosphorus signal suggested the decomposition of 7-phosphanorbornadiene molybdenum(o) complex **58**.

Scheme 3.40 Attempted Decomplexation of Benzo-7-Phenyl-7-Phosphanorbornadiene Molybdenum(0) Complex

3.3 Conclusion

In this chapter, we have highlighted a new molecular scaffold for the generation of terminal phosphinidene complexes. However, the high stability of these complexes prohibits their widespread utilization, despite the much easier synthesis and purification when compared to using DMAD as a dienophile.

This stability, though generally undesirable, can be exploited. Preliminary results have been observed with the generation of phosphinidene iron(0) complexes, and we believe that if the conditions can be optimised, the decomplexation of the benzo-7-phosphanorbornadiene metal complexes can be achieved. This would present a molecule, which could serve as a precursor to “free” phosphinidenes under relatively mild conditions. Furthermore, as a matter of spin conservation, these phosphinidenes would be singlet in nature, allowing for greater control over their reactivity.

3.4 Experimental Details

3.4.1 General Considerations

All reactions with air- or moisture-sensitive manipulations were carried out under positive pressure of nitrogen using standard Schlenk techniques. Tetrahydrofuran was distilled from sodium-benzophenone, toluene was

distilled from sodium, dichloromethane was distilled from phosphorus pentoxide and hexane was distilled from sodium. All other solvents were used as received. Column chromatography was performed on silica gel (40-63 microns). NMR spectra were recorded on a Bruker Avance 500 spectrometer (500 MHz for ^1H , 125 MHz for ^{13}C , 202 MHz for ^{31}P), Bruker Avance 400 spectrometer (400 MHz for ^1H , 100 MHz for ^{13}C , 162 MHz for ^{31}P), Bruker Avance 300 spectrometer (300 MHz for ^1H , 75 MHz for ^{13}C , 121 MHz for ^{31}P), Bruker Avance III 400 spectrometer (400 MHz for ^1H , 100 MHz for ^{13}C , 162 MHz for ^{31}P) or JEOL ECA400 spectrometer (400 MHz for ^1H , 100 MHz for ^{13}C , 162 MHz for ^{31}P). Chemical shifts are reported in δ (ppm), referenced to the residual solvent resonance of d_2 -dichloromethane for ^1H NMR ($\delta = 5.32$) and ^{13}C NMR ($\delta = 53.84$ ppm) or CDCl_3 for ^1H NMR ($\delta = 7.26$) and ^{13}C NMR ($\delta = 77.00$). ^{31}P chemical shifts are referenced to an external standard of 85% H_3PO_4 in H_2O ($\delta = 0.00$) and are uncorrected. Multiplicities are given as: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), m (multiplet). The number of protons (n) for a given resonance are given by nH and coupling constants are given as a J value in Hz. Mass spectra were recorded on a JEOL AccuTOF-DART HRMS.

Experimental Procedures

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3,4-Dimethyl-1-phenylphosphole pentacarbonyltungsten(o) (**24**)

Tungsten(o) hexacarbonyl (1.93 g, 5.5 mmol) was dissolved in acetonitrile and trimethylamine N-oxide dihydrate (0.611 g, 5.5 mmol) was added and stirred for 3 hours at room temperature. After which, it was evaporated to dryness under reduced pressure, redissolved in THF (20 mL) and **17** (1 mL, 5.5 mmol) was added and stirred for 14 hours at room temperature. Chromatography over silica gel at -10 °C with hexanes yielded the pale yellow solid.

$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz): δ 10.68 (s, $^1\text{J}_{\text{P-W}} = 215$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 16.98 (d, $^3\text{J}_{\text{P-C}} = 11.5$ Hz, 2C, -CH₃), 129.02 (d, $^3\text{J}_{\text{P-C}} = 10.5$ Hz, 2C, Ar-C), 130.19 (d, $^1\text{J}_{\text{P-C}} = 44.1$ Hz, 2C, Ar-C), 130.59 (d, $^4\text{J}_{\text{P-C}} = 1.9$ Hz, 1C, Ar-C), 130.92 (d, $^2\text{J}_{\text{P-C}} = 41.2$ Hz, 2C, C-CH₃), 131.48 (d, $^1\text{J}_{\text{P-C}} = 12.4$ Hz, 2C, P-C), 150.37 (d, $^1\text{J}_{\text{P-C}} = 8.6$ Hz, 1C, Ar-C), 196.15 (d, $^2\text{J}_{\text{P-C}} = 6.7$ Hz, 4C, *cis*-CO), 198.98 (d, $^2\text{J}_{\text{P-C}} = 18.1$ Hz, 1C, *trans*-CO); ^1H NMR (CDCl_3 , 400 MHz): δ 2.29 (s, 6H, -CH₃), 6.64 (d, $^2\text{J}_{\text{P-H}} = 38.1$ Hz, 2H, PCH), 7.46-7.50 (m, 3H, Ar-H), 7.61-7.66 (m, 2H, Ar-H)

(2,3-Dimethyl-9-phenyl-1,4,4a,8a-tetrahydro-1,4-phosphanonaphthalense-5,8-dione pentacarbonyltungsten(o) (**25**))

24 (2.5600 g, 5.0 mmol) and *p*-benzoquinone (1.6200 g, 15.0 mmol) were dissolved in toluene (20 mL) and heated at 80 °C for 60 hours under inert conditions. The resulting solution was concentrated after cooling to room temperature, and the product was precipitated by the addition of hexane. The solids were collected and washed with hexane and dried under reduced pressure, yielding a yellow powder (2.7917 g, 90 % yield).

$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 162 MHz): δ 51.67 (s, $^1\text{J}_{\text{P-W}} = 241$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100 MHz): δ 15.91 (d, $^3\text{J}_{\text{P-C}} = 2.7$ Hz, 2C, CH_3), 48.70 (d, $^2\text{J}_{\text{P-C}} = 4.9$ Hz, 2C, CH-CO), 54.78 (d, $^1\text{J}_{\text{P-C}} = 24.3$ Hz, 2C, P-CH), 127.97 (d, $^2\text{J}_{\text{P-C}} = 9.4$ Hz, 2C, Ar-C), 129.97 (d, $^3\text{J}_{\text{P-C}} = 7.3$ Hz, 2C, Ar-C), 130.43 (s, 1C, Ar-C), 135.66 (d, $^2\text{J}_{\text{P-C}} = 13.0$ Hz, 2C, C-CH_3), 140.49 (d, $^2\text{J}_{\text{P-C}} = 13.8$ Hz, 1C, Ar-C), 142.28 (s, 2C, C=CH), 196.33 (d, $^2\text{J}_{\text{P-C}} = 6.9$ Hz, 4C, *cis*-CO), 197.66 (d, $^3\text{J}_{\text{P-C}} = 6.6$ Hz, 2C, C=O), 198.94 (d, $^2\text{J}_{\text{P-C}} = 25.3$ Hz, 1C, *trans*-CO); ^1H NMR (CD_2Cl_2 , 400 MHz): δ 1.74 (s, 6H, $-\text{CH}_3$), 3.34 (s, 2H, HC-CO), 3.74 (d, $^2\text{J}_{\text{P-H}} = 4.4$ Hz, 2H, PCH), 6.63 (s, 2H, C=CH), 7.34-7.41 (m, 3H, Ar-H), 7.48-7.52 (m, 2H, Ar-H)

HRMS m/z : 620.0220 (calcd. for $\text{C}_{23}\text{H}_{17}\text{O}_7\text{P}^{184}\text{W}$: 620.0221)

26

Methoxy(phenyl)phosphine pentacarbonyltungsten(o) (**26**)

25 was dissolved in THF and sodium methoxide was added at room temperature and stirred for 16 hours. Solvent was removed, and product was purified *via* column chromatography on silica gel at -10 °C.

$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 121 MHz): δ 107.77 (s, $^1J_{\text{P-W}} = 276$ Hz); ^{31}P NMR (CD_2Cl_2 , 121 MHz): δ 107.77 (dq, $^1J_{\text{P-H}} = 347$ Hz, $^3J_{\text{P-H}} = 12.6$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 75 MHz): δ 60.31 (d, $^2J_{\text{P-C}} = 14.4$ Hz, 1C, O-CH₃), 129.46 (d, $^3J_{\text{P-C}} = 9.2$ Hz, 2C, Ar-C), 130.86 (d, $^2J_{\text{P-C}} = 11.9$ Hz, 2C, Ar-C), 131.99 (s, 1C, Ar-C), 135.19 (d, $^1J_{\text{P-C}} = 40.7$ Hz, 1C, Ar-C), 196.13 (d, $^2J_{\text{P-C}} = 8.0$ Hz, 4C, *cis*-CO), 200.04 (d, $^2J_{\text{P-C}} = 25.5$ Hz, 1C, *trans*-CO); ^1H NMR (CD_2Cl_2 , 300 MHz): δ 3.52 (d, $^3J_{\text{P-H}} = 12.6$ Hz, 3H, O-CH₃), 7.54-7.65 (m, 5H, Ar-H), 7.89 (d, $^1J_{\text{P-H}} = 346.5$ Hz, 1H, P-H)

27

2,3-Dimethyl-9-phenyl-1,4-dihydro-1,4-phosphanonaphthalene-5,8-diol
pentacarbonyltungsten(o) (**27**)

$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 202 MHz): δ 168.57 (s, $^1J_{\text{PW}} = 230$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 125 MHz): δ 15.94 (d, $^3J_{\text{P-C}} = 2.5$ Hz, 2C, -CH₃), 53.80 (d, $^1J_{\text{P-C}} =$

22.5 Hz, 2C, P-C), 114.27 (s, 2C, C=CH), 128.46 (d, $^2J_{P-C}$ = 16.9 Hz, 2C, Ar-C), 128.47 (s, 2C, Ar-C), 129.14 (s, 1C, Ar-C), 132.59 (d, $^2J_{P-C}$ = 4.4 Hz, 2C, P-CH-C-COCH₃), 138.87 (d, $^2J_{P-C}$ = 15.6 Hz, 2C, C-CH₃), 141.94 (d, $^1J_{P-C}$ = 15.6 Hz, 1C, Ar-C), 145.30 (d, $^3J_{P-C}$ = 3.6 Hz, 2C, C-OH), 196.81 (d, $^2J_{P-C}$ = 6.9 Hz, 4C, *cis*-CO), 199.74 (d, $^2J_{P-C}$ = 24.4 Hz, 1C, *trans*-CO); 1H NMR (CD₂Cl₂, 500 MHz): δ 2.03 (s, 6H, -CH₃), 4.24 (s, 2H, PCH), 4.57 (brs, 2H, OH), 6.14 (s, 2H, C=CH), 7.07-7.10 (m, 2H, Ar-H), 7.16-7.25 (m, 3H, Ar-H)

HRMS *m/z*: 620.0212 (calcd. for C₂₃H₁₇O₇P¹⁸⁴W: 620.0221)

5,8-Dimethoxy-2,3-dimethyl-9-phenyl-1,4-dihydro-1,4-phosphanonaphthalene pentacarbonyltungsten(o) (**28**)

28 (1.2400 g, 2.0 mmol) was dissolved in THF (30 mL). LDA (4.0 mmol) in THF (2 mL) was added dropwise at room temperature and the mixture was stirred for 10 min. Methyl triflate (0.44 mL, 4.0 mmol) was then added and stirred for 30 min. After removal of solvent under reduced pressure, the crude mixture was dissolved in a mixture of dichloromethane and hexane, and purified over silica at -10 °C, yielding a cream coloured solid (0.5545 g, 43 %).

$^{31}P\{^1H\}$ NMR (CD₂Cl₂, 162 MHz): δ 172.65 (s, $^1J_{P-W}$ = 231 Hz); $^{13}C\{^1H\}$ NMR (CD₂Cl₂, 100 MHz): δ 15.89 (d, $^3J_{P-C}$ = 2.9 Hz, 2C, -CH₃), 53.94 (d, $^1J_{P-C}$ = 23.0 Hz, 2C, P-C), 56.70 (s, 2C, O-CH₃), 110.14 (s, 2C, C=CH), 128.40 (s, 2C,

Ar-C), 128.41 (d, $^2J_{P-C} = 16.0$ Hz, 2C, Ar-C), 129.04 (s, 1C, Ar-C), 134.90 (d, $^2J_{P-C} = 4.8$ Hz, 2C, P-CH-C-COCH₃), 139.05 (d, $^2J_{P-C} = 16.2$ Hz, 2C, C-CH₃), 142.15 (d, $^1J_{P-C} = 15.5$ Hz, 1C, Ar-C), 149.96 (d, $^3J_{P-C} = 3.4$ Hz, 2C, C-OCH₃), 196.89 (d, $^2J_{P-C} = 6.8$ Hz, 4C, *cis*-CO), 199.87 (d, $^2J_{P-C} = 24.3$ Hz, 1C, *trans*-CO); 1H NMR (CD₂Cl₂, 400 MHz): δ 2.02 (s, 6H, -CH₃), 3.69 (s, 6H, O-CH₃), 4.27 (d, $^2J_{P-H} = 2.4$ Hz, 2H, PCH), 6.33 (s, 2H, C=CH), 7.02-7.06 (m, 2H, Ar-H), 7.11-7.21 (m, 3H, Ar-H)

HRMS *m/z*: 648.0546 (calcd. for C₂₅H₂₁O₇P¹⁸⁴W: 648.0534)

29

1,2,3-Triphenylphosphirene pentacarbonyltungsten(o) (**29**)

28 (0.1296 g, 0.2 mmol) and diphenylacetylene (0.1068 g, 0.6 mmol) were dissolved in toluene (1 mL). Copper(I) chloride (0.0198 g, 0.2 mmol) was added and the reaction mixture was heated at 70 °C for 2 hours. The crude mixture was purified over silica gel at -10 °C using hexane as the eluent, yielding a cream coloured solid (0.0304 g, 25 %).

$^{31}P\{^1H\}$ NMR (CDCl₃, 121 MHz): δ -159.99 (s, $^1J_{P-W} = 267$ Hz); $^{13}C\{^1H\}$ NMR (CDCl₃, 75 MHz): δ 127.21 (d, $^3J_{P-C} = 6.8$ Hz, 2C, Ar-C), 128.27 (d, $^2J_{P-C} = 9.3$ Hz, 2C, Ar-C), 128.58 (d, $^2J_{P-C} = 10.4$ Hz, 2C, Ar-C), 129.34 (s, 2C, Ar-C), 130.37 (d, $^3J_{P-C} = 5.2$ Hz, 4C, Ar-C), 130.53 (d, $^4J_{P-C} = 2.2$ Hz, 4C, Ar-C), 130.66 (s, 1C, Ar-C), 131.30 (d, $^1J_{P-C} = 15.8$ Hz, 2C, Ar-C), 137.53 (d, $^2J_{P-C} = 6.1$ Hz, 1C, Ar-C), 195.94 (d, $^2J_{P-C} = 8.4$ Hz, 4C, *cis*-CO), 197.74 (d, $^2J_{P-C} =$

31.0 Hz, 1C, *trans*-CO); ^1H NMR (CDCl_3 , 300 MHz): δ 7.37-7.57 (m, 11H, Ar-H), 7.91-7.93 (m, 4H, Ar-H)

30

1,4-Dimethoxy-6,7-dimethylnaphthalene (**30**)

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 20.27 (s, 2C, $-\text{CH}_3$), 55.65 (s, 2C, $-\text{OCH}_3$), 102.34 (s, 2C, Ar-C), 121.43 (s, 2C, Ar-C), 125.07 (s, 2C, Ar-C), 135.47 (s, 2C, Ar-C), 149.12 (s, 2C, Ar-C); ^1H NMR (CDCl_3 , 400 MHz): δ 2.45 (s, 6H, $-\text{CH}_3$), 3.96 (s, 6H, $-\text{OCH}_3$), 6.62 (s, 2H, Ar-H), 7.97 (s, 2H, Ar-H)

HRMS m/z : 216.1146 (calcd. for $\text{C}_{14}\text{H}_{16}\text{O}_2$: 216.1150)

31

1,2,3-Triphenylphosphirane pentacarbonyltungsten(o) (**31**)

28 (0.1296 g, 0.2 mmol) and *trans*-stilbene (0.1080 g, 0.6 mmol) were dissolved in toluene (1 mL). Copper(I) chloride (0.0198 g, 0.2 mmol) was added and the reaction mixture was heated at 70 °C for 2 hours. The crude mixture was purified over silica gel at -10 °C using hexane as the eluent, yielding a cream coloured solid (0.0677 g, 55 %).

$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 202 MHz): δ -118.97 (s, $^1J_{\text{P-W}} = 230$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz): δ 33.13 (d, $^1J_{\text{P-C}} = 15.1$ Hz, 1C, P-CH), 35.99 (d, $^1J_{\text{P-C}} = 18.6$ Hz, 1C, P-CH), 126.74 (s, 1C, Ar-C), 127.52 (s, 2C, Ar-C), 127.63 (s, 1C, Ar-C), 128.38 (s, 2C, Ar-C), 128.53 (d, $^3J_{\text{P-C}} = 9.3$ Hz, 2C, Ar-C), 128.92 (d, $^3J_{\text{P-C}} = 5.3$ Hz, 2C, Ar-C), 129.04 (s, 2C, Ar-C), 130.17 (s, 1C, Ar-C), 132.70 (d, $^2J_{\text{P-C}} = 10.1$ Hz, 2C, Ar-C), 132.92 (s, 1C, Ar-C), 134.63 (d, $^2J_{\text{P-C}} = 5.3$ Hz, 1C, Ar-C), 136.07 (s, 1C, Ar-C), 195.05 (d, $^2J_{\text{P-C}} = 7.9$ Hz, 4C, *cis*-CO), 197.68 (d, $^2J_{\text{P-C}} = 31.9$ Hz, 1C, *trans*-CO); ^1H NMR (CDCl_3 , 500 MHz): δ 3.54-3.57 (m, 1H, PC-H), 3.92-3.97 (m, 1H, PC-H), 7.01-7.13 (m, 5H, Ar-C), 7.22-7.47 (m, 10H, Ar-C).

32

3,4-Dimethyl-1-phenylphospholene pentacarbonyltungsten(o) (**32**)

28 (0.1296 g, 0.2 mmol) and 2,3-dimethylbutadiene (0.1068 g, 0.6 mmol) were dissolved in toluene (1 mL). Copper(I) chloride (0.0198 g, 0.2 mmol) was added and the reaction mixture was heated at 110 °C for 2 hours. The crude mixture was purified over silica gel at -10 °C using hexane as the eluent, yielding a cream coloured solid (0.0243 g, 24 %).

$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz): δ -3.32 (s, $^1J_{\text{P-W}} = 231$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 16.16 (d, $^3J_{\text{P-C}} = 7.7$ Hz, 2C, -CH₃), 44.47 (d, $^1J_{\text{P-C}} = 27.4$ Hz, 2C, P-CH₂), 128.70 (d, $^3J_{\text{P-C}} = 9.2$ Hz, 2C, Ar-C), 129.37 (d, $^2J_{\text{P-C}} = 10.7$ Hz, 2C, Ar-C), 129.78 (s, 2C, Ar-C, C=C), 137.76 (d, $^1J_{\text{P-C}} = 34.5$ Hz, 1C, Ar-C),

195.05 (d, $^2J_{P-C} = 7.2$ Hz, 4C, *cis*-CO), 199.75 (d, $^2J_{P-C} = 20.6$ Hz, 1C, *trans*-CO); 1H NMR (CDCl₃, 400 MHz): δ 1.74 (s, 6H, -CH₃), 3.12 (s, 4H, P-CH₂), 7.36-7.51 (m, 5H, Ar-H)

HRMS m/z: 514.0155 (calcd. for C₁₇H₁₅O₅P¹⁸⁴W: 514.0167)

33

1,3,4-Trimethylphosphole pentacarbonyltungsten(o) (**33**)

To a solution of **15** (from 5.5 mmol of **17**) in THF was added methyl iodide (1.25 mL, 20 mmol) and stirred at room temperature for 2 hours. Evaporation of solvent and chromatography over silica gel at -10 °C with hexanes gave **33** as a pale yellow solid.

$^{31}P\{^1H\}$ NMR (CDCl₃, 162 MHz): δ -7.78 (s, $^1J_{P-W} = 209$ Hz); $^{13}C\{^1H\}$ NMR (CDCl₃, 100 MHz): δ 15.13 (d, $^1J_{P-C} = 27.0$ Hz, 1C, P-CH₃), 17.19 (d, $^3J_{P-C} = 12.0$ Hz, 2C, C-CH₃), 130.62 (d, $^1J_{P-C} = 42.0$ Hz, 2C, P-C), 150.14 (d, $^2J_{P-C} = 8.0$ Hz, 2C, P-C-C), 196.28 (d, $^2J_{P-C} = 7.0$ Hz, 4C, *cis*-CO), 199.44 (d, $^2J_{P-C} = 18.0$ Hz, 1C, *trans*-CO); 1H NMR (CDCl₃, 400 MHz): δ 1.70 (d, $^1J_{P-H} = 8.8$ Hz, 3H, PCH₃), 2.14 (s, 6H, -PCC-CH₃), 6.35 (d, $^2J_{P-H} = 37.2$ Hz, 2H, PCH)

34

2,3,9-Trimethyl-1,4,4a,8a-tetrahydro-1,4-phosphanonaphthalene-5,8-dione pentacarbonyltungsten(o) (**34**)

33 (0.9000 g, 2.0 mmol) and *p*-benzoquinone (0.6480 g, 6.0 mmol) were dissolved in toluene (10 mL) and heated at 80 °C for 60 hours under inert conditions. The resulting solution was concentrated after cooling to room temperature, and the product was precipitated by the addition of hexane. The solids were collected and washed with hexane and dried under reduced pressure, yielding a pale-yellow powder (0.6169 g, 55 % yield).

$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz): δ 39.04 (s, $^1J_{\text{P-W}} = 247$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 15.53 (d, $^3J_{\text{P-C}} = 2.8$ Hz, 2C, -CH₃), 20.49 (d, $^2J_{\text{P-C}} = 2.2$ Hz, 2C, P-CH-CH), 47.79 (d, $^1J_{\text{P-C}} = 4.7$ Hz, 1C, P-CH₃), 54.82 (d, $^1J_{\text{P-C}} = 24.6$ Hz, 2C, P-CH), 136.21 (d, $^2J_{\text{P-C}} = 12.3$ Hz, 2C, C-CH₃), 141.86 (s, 2C, C=CH), 195.95 (d, $^2J_{\text{P-C}} = 6.8$ Hz, 4C, *cis*-CO), 197.01 (d, $^3J_{\text{P-C}} = 6.1$ Hz, 2C, C=O), 197.70 (d, $^2J_{\text{P-C}} = 25.3$ Hz, 1C, *trans*-CO); ^1H NMR (CDCl_3 , 400 MHz): δ 1.65 (d, $^4J_{\text{P-H}} = 1.2$ Hz, 6H, C-CH₃), 1.70 (d, $^2J_{\text{P-H}} = 5.6$ Hz, 3H, P-CH₃), 3.29 (d, $^2J_{\text{P-H}} = 4.8$ Hz, 2H, PCH), 3.58 (s, 2H, PCH-CH), 6.70 (s, 2H, C=CH)

HRMS *m/z*: 558.0067 (calcd. for C₁₈H₁₅O₇P¹⁸⁴W: 558.0065)

5,8-Dimethoxy-2,3,9-trimethyl-1,4-dihydro-1,4-phosphanonaphthalene
pentacarbonyltungsten(o) (**35**)

34 (0.5580 g, 1.0 mmol) was dissolved in THF (15 mL). LDA (2.0 mmol) in THF (2 mL) was added dropwise at room temperature and the mixture was stirred for 10 min. Methyl triflate (0.22 mL, 2.0 mmol) was then added and stirred for 30 min. After removal of solvent under reduced pressure, the crude mixture was dissolved in a mixture of dichloromethane and hexane, and purified over silica at -10 °C, yielding a pale-yellow solid (0.0893 g, 15 %).

$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 121 MHz): δ 158.78 (s, $^1J_{\text{P-W}} = 229$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz): δ 15.59 (d, $^3J_{\text{P-C}} = 3.0$ Hz, 2C, C- CH_3), 21.30 (d, $^1J_{\text{P-C}} = 4.7$ Hz, 1C, P- CH_3), 53.81 (d, $^1J_{\text{P-C}} = 23.5$ Hz, 1C, P-CH), 56.27 (s, 2C, O- CH_3), 109.99 (s, 2C, C=CH), 134.05 (d, $^2J_{\text{P-C}} = 4.7$ Hz, 2C, C- CH_3), 139.36 (d, $^2J_{\text{P-C}} = 15.8$ Hz, 2C, P-CH-C-COCH $_3$), 149.88 (d, $^3J_{\text{P-C}} = 3.4$ Hz, 2C, C-OCH $_3$), 196.57 (d, $^2J_{\text{P-C}} = 6.7$ Hz, 4C, *cis*-CO), 198.78 (d, $^2J_{\text{P-C}} = 24.0$ Hz, 1C, *trans*-CO); ^1H NMR (CDCl_3 , 300 MHz): δ 1.31 (d, $^2J_{\text{P-H}} = 5.1$ Hz, 3H, P- CH_3), 1.94 (d, $^4J_{\text{P-H}} = 1.5$ Hz, 3H, C- CH_3), 3.81 (s, 6H, O- CH_3), 3.85 (d, $^2J_{\text{P-H}} = 3.0$ Hz, 2H, PCH), 6.64 (s, 2H, C=CH).

41

N,N-(diphenyl)amino-3,4-dimethylphosphole pentacarbonyltungsten(o)
(**41**)

To a THF solution of **14** (from 5.5 mmol of **17**) was added lithium diphenylamide (4.0 mmol) at 0 °C and stirred for 3 hours. After which, the solution was concentrated and purified by column chromatography over silica at -10 °C yielding **41**.

$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 121 MHz): δ 61.08 (s, $^1J_{\text{P-W}} = 240$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz): δ 16.46 (d, $^3J_{\text{P-C}} = 9.7$ Hz, 2C, -CH₃), 125.56 (s, 2C, Ar-C), 127.21 (d, $^3J_{\text{P-C}} = 4.7$ Hz, 4C, Ar-C), 128.83 (s, 4C, Ar-C), 129.07 (d, $^1J_{\text{P-C}} = 44.9$ Hz, 2C, P-C), 146.65 (d, $^2J_{\text{P-C}} = 3.0$ Hz, 2C, C-CH₃), 148.20 (d, $^2J_{\text{P-C}} = 12.0$ Hz, 4C, Ar-C), 196.08 (d, $^2J_{\text{P-C}} = 6.0$ Hz, 4C, *cis*-CO), 198.44 (d, $^2J_{\text{P-C}} = 21.0$ Hz, 1C, *trans*-CO); ^1H NMR (CDCl_3 , 300 MHz): δ 1.94 (s, 6H, -CH₃), 6.26 (d, $^2J_{\text{P-H}} = 36.0$ Hz 2H, P-CH), 7.10-7.27 (m, 10H, Ar-H)

42

(2,3-Dimethyl-9-(diphenylamino)-1,4,4a,8a-tetrahydro-1,4-phosphanonaphthalene-5,8-dione pentacarbonyltungsten(o) (**42**)

41 and *p*-benzoquinone were dissolved in toluene (20 mL) and heated at 80 °C for 60 hours under inert conditions. The resulting solution was concentrated after cooling to room temperature, and the product was precipitated by the addition of hexane. The solids were collected and washed with hexane and dried under reduced pressure, yielding a yellow powder.

$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz): δ 76.87 (s, $^1J_{\text{P-W}} = 272$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 16.13 (s, 2C, $-\text{CH}_3$), 47.78 (d, $^2J_{\text{P-C}} = 6.48$ Hz, 2C, PC-CH-CO), 59.49 (d, $^1J_{\text{P-C}} = 32.4$ Hz, 2C, P-CH), 124.46 (d, $^3J_{\text{P-C}} = 4.9$ Hz, 4C, Ar-C), 125.17 (s, 2C, Ar-C), 129.91 (s, 4C, Ar-C), 134.83 (d, $^2J_{\text{P-C}} = 25.9$ Hz, 2C, Ar-C), 141.97 (s, 2C, $\text{C}=\text{CH}$), 144.99 (d, $^2J_{\text{P-C}} = 4.9$ Hz, 2C, $\text{C}=\text{C}-\text{CH}_3$), 195.83 (d, $^2J_{\text{P-C}} = 11.8$ Hz, 4C, *cis*-CO), 196.69 (d, $^2J_{\text{P-C}} = 50.7$ Hz, 1C, *trans*-CO), 197.49 (d, $^3J_{\text{P-C}} = 9.9$ Hz, 2C, $\text{C}=\text{O}$); ^1H NMR (CD_2Cl_2 , 400 MHz): δ 1.98 (d, $^4J_{\text{P-H}} = 0.8$ Hz 6H, $-\text{CH}_3$), 3.34 (s, 2H, HC-CO), 3.58 (s, 2H, PCH), 6.64 (s, 2H, $\text{C}=\text{CH}$), 7.07-7.36 (m, 3H, Ar-H)

3,4-Dimethyl-1-phenylphosphole sulfide (**45**)

17 was dissolved in dichloromethane. Sulfur (2 eqv.) was added, along with one drop of N-methylimidazole. The reaction was refluxed for 14 hours. The mixture was concentrated and purified by column chromatography over silica gel with dichloromethane, yielding a pale cream solid.

$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz): δ 46.20 (s); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 17.14 (d, $^3\text{J}_{\text{P-C}} = 8.0$ Hz, 2C, -CH₃), 125.32 (d, $^1\text{J}_{\text{P-C}} = 82.1$ Hz, 2C, P-CH), 127.41 (d, $^1\text{J}_{\text{P-C}} = 78.8$ Hz, 1C, Ar-C), 128.30 (d, $^2\text{J}_{\text{P-C}} = 12.6$ Hz, 2C, Ar-C), 130.04 (d, $^3\text{J}_{\text{P-C}} = 11.6$ Hz, 2C, Ar-C), 131.52 (d, $^4\text{J}_{\text{P-C}} = 2.9$ Hz, 1C, Ar-C), 153.36 (d, $^1\text{J}_{\text{P-C}} = 17.0$ Hz, 1C, Ar-C); ^1H NMR (CDCl_3 , 400 MHz): δ 2.02 (s, 6H, -CH₃), 6.01 (d, $^2\text{J}_{\text{P-H}} = 30.8$ Hz, 2H, PCH), 7.31-7.38 (m, 3H, Ar-H), 7.71-7.76 (m, 2H, Ar-H)

2,3-Dimethyl-9-phenyl-1,4,4a,8a-tetrahydro-1,4-phosphanonaphthalene-5,8-dione-9-sulfide (**46**)

45 (2.2000 g, 10.0 mmol) and *p*-benzoquinone (3.2400 g, 30.0 mmol) were dissolved in toluene (50 mL) and heated at 80 °C for 60 hours under inert conditions. The resulting solution was run through a short silica column

after cooling to room temperature and the yellow band was collected and concentrated. The product was precipitated with hexane, and the solids were collected and washed with hexane to obtain a grey powder (2.0029 g, 61 %).

$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz): δ 93.92 (s); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 15.28 (d, $^3J_{\text{P-C}} = 3.2$ Hz, 2C, C- CH_3), 47.41 (d, $^2J_{\text{P-C}} = 18.1$ Hz, 2C, P-CH-CH), 54.29 (d, $^1J_{\text{P-C}} = 51.2$ Hz, 2C, P-CH), 128.77 (d, $^2J_{\text{P-C}} = 12.0$ Hz, 2C, Ar-C), 129.92 (d, $^1J_{\text{P-C}} = 82.3$ Hz, 1C, Ar-C), 130.04 (d, $^3J_{\text{P-C}} = 9.7$ Hz, 2C, Ar-C), 131.38 (d, $^4J_{\text{P-C}} = 2.9$ Hz, 1C, Ar-C), 133.96 (d, $^2J_{\text{P-C}} = 6.7$ Hz, 2C, C- CH_3), 142.42 (d, $^4J_{\text{P-C}} = 2.9$ Hz, 2C, C=CH), 196.96 (d, $J_{\text{P-C}} = 14.1$ Hz, 2C, C=O); ^1H NMR (CDCl_3 , 400 MHz): δ 1.43 (d, $^4J_{\text{P-H}} = 2.0$ Hz, 6H, C- CH_3), 3.58-3.61 (m, 2H, P-CH), 4.25 (d, $^2J_{\text{P-H}} = 4.8$ Hz, 2H, PCH-CH), 6.74 (s, 2H, C=CH), 7.39-7.46 (m, 3H, Ar-H), 7.51-7.57 (m, 2H, Ar-H).

HRMS m/z : 328.0691 (calcd. for $\text{C}_{18}\text{H}_{17}\text{O}_2\text{PS}$: 328.0687).

47

3,4-Dimethyl-1-phenylphosphole tetracarbonyliron(0) (**47**)

17 (2 mL, 11.0 mmol) was dissolved in THF (20 mL). Diiron(0) nonacarbonyl (4.00 g, 11.0 mmol) was added and stirred for 16 hours. After evaporation of solvent, the crude mixture was chromatographed over silica, yielding **47** as a bright yellow solid (3.2372 g, 83%).

$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz): δ 65.40 (s); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 17.22 (d, $^3J_{\text{P-C}} = 13.0$ Hz, 2C, - CH_3), 128.15 (d, $^3J_{\text{P-C}} = 10.5$ Hz, 2C,

Ar-C), 128.76 (d, $^2J_{P-C} = 10.1$ Hz, 2C, Ar-C), 130.05 (d, $^1J_{P-C} = 50.1$ Hz, 2C, P-CH), 131.04 (s, 1C, Ar-C), 131.73 (d, $^3J_{P-C} = 11.4$ Hz, 2C, Ar-C), 150.28 (d, $^1J_{P-C} = 10.0$ Hz, 1C, Ar-C), 213.15 (d, $^2J_{P-C} = 19.0$ Hz, 4C, CO); 1H NMR ($CDCl_3$, 400 MHz): δ 2.15 (s, 6H, $-CH_3$), 6.49 (d, $^2J_{P-H} = 35.2$ Hz, 2H, PCH), 7.40-7.42 (m, 3H, Ar-H), 7.59-7.65 (m, 2H, Ar-H)

49

6,7-Dimethylnaphthalene-1,4-dione (**49**)

$^{13}C\{^1H\}$ NMR (CD_2Cl_2 , 100 MHz): δ 20.38 (s, 2C, $-CH_3$), 127.55 (s, 2C, $C=C$), 130.45 (s, 2C, Ar-C), 138.92 (s, 2C, Ar-C), 144.35 (s, 2C, Ar-C), 185.66 (s, 2C, CO); 1H NMR (CD_2Cl_2 , 400 MHz): δ 2.41 (s, 6H, $-CH_3$), 6.88 (s, 2H, $C=CH$), 7.81 (s, 2H, Ar-H)

56

3,4-Dimethyl-1-phenylphosphole pentacarbonylmolybdenum(o) (**56**)

17 (5.5 mmol), trimethylamine N-oxide dihydrate (0.611 g, 5.5 mmol) and molybdenum(o) hexacarbonyl (1.452 g, 5.5 mmol) were dissolved in DCM and refluxed for 6 hours. The mixture was concentrated and chromatographed over silica with hexanes at -10 °C, yielding a pale yellow solid.

$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz): δ 29.90 (s); ^1H NMR (CDCl_3 , 400 MHz): δ 2.24 (s, 6H, $-\text{CH}_3$), 6.64 (d, $^2J_{\text{P-H}} = 37.0$ Hz, 2H, PCH), 7.44-7.46 (m, 3H, Ar-*H*), 7.58-7.63 (m, 2H, Ar-*H*)

57

(2,3-Dimethyl-9-phenyl-1,4,4a,8a-tetrahydro-1,4-phosphanonaphthalene-5,8-dione pentacarbonylmolybdenum(o) (**57**)

56 (0.8480 g, 2.0 mmol) and *p*-benzoquinone (0.6480 g, 6.0 mmol) were dissolved in toluene (10 mL) and heated at 80 °C for 60 hours under inert conditions. The resulting solution was concentrated after cooling to room temperature and the product was precipitated by the addition of hexane. The

solids were collected and washed with hexane and dried under reduced pressure, yielding a pale-yellow powder (0.6622 g, 62 % yield).

$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz): δ 71.70 (s); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 15.63 (d, $^3J_{\text{P-C}} = 2.5$ Hz, $-\text{CH}_3$), 48.45 (d, $^2J_{\text{P-C}} = 4.0$ Hz, CH-CO), 54.04 (d, $^1J_{\text{P-C}} = 19.8$ Hz, P-CH), 127.41 (d, $^2J_{\text{P-C}} = 9.6$ Hz, 2C, Ar-C), 129.67 (d, $^3J_{\text{P-C}} = 6.9$ Hz, 2C, Ar-C), 129.80 (s, 1C, Ar-C), 135.09 (d, $^2J_{\text{P-C}} = 13.0$ Hz, 2C, C-CH_3), 140.26 (d, $^2J_{\text{P-C}} = 8.0$ Hz, 1C, Ar-C), 141.85 (s, 2C, C=CH), 197.59 (d, $^2J_{\text{P-C}} = 5.7$ Hz, 4C, *cis*-CO), 204.81 (d, $^3J_{\text{P-C}} = 9.1$ Hz, 2C, C=O), 208.65 (d, $^2J_{\text{P-C}} = 26.7$ Hz, 1C, *trans*-CO); ^1H NMR (CDCl_3 , 400 MHz): δ 1.74 (s, 6H, $-\text{CH}_3$), 3.33 (s, 2H, HC-CO), 3.68 (d, $^2J_{\text{PH}} = 5.2$ Hz, 2H, PCH), 6.64 (s, 2H, C=CH), 7.30-7.39 (m, 3H, Ar-H), 7.44-7.48 (m, 2H, Ar-H)

HRMS m/z : 533.9760 (calcd. for $\text{C}_{23}\text{H}_{17}\text{NO}_7\text{PMo}$: 533.9766)

5,8-Dimethoxy-2,3-dimethyl-9-phenyl-1,4-dihydro-1,4-phosphanonaphthalene pentacarbonylmolybdenum(o) (**58**)

57 (0.5600 g, 1.0 mmol) was dissolved in THF (15 mL). LDA (2.0 mmol) in THF (2 mL) was added dropwise at room temperature and the mixture was stirred for 10 min. Methyl triflate (0.22 mL, 2.0 mmol) was then added and stirred for 30 min. After removal of solvent under reduced pressure, the crude mixture was dissolved in a mixture of dichloromethane and hexane, and purified over silica at -10 °C, yielding a pale-yellow solid.

$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz): δ 199.66 (s); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 15.68 (d, $^3J_{\text{P-C}} = 2.6$ Hz, 2C, $-\text{CH}_3$), 53.25 (d, $^1J_{\text{P-C}} = 19.0$ Hz, 2C, P-C), 56.32 (s, 2C, O- CH_3), 109.67 (s, 2C, C=CH), 127.94 (d, $^2J_{\text{P-C}} = 7.5$ Hz, 2C, Ar-C), 128.37 (s, 1C, Ar-C), 135.00 (d, $^3J_{\text{P-C}} = 3.7$ Hz, 2C, Ar-C), 138.56 (d, $^2J_{\text{P-C}} = 16.4$ Hz, 2C, C- CH_3), 141.61 (d, $^1J_{\text{P-C}} = 9.5$ Hz, 1C, Ar-C), 149.47 (d, $J_{\text{P-C}} = 3.1$ Hz, 2C, C-O CH_3), 205.25 (d, $^2J_{\text{P-C}} = 8.7$ Hz, 4C, *cis*-CO), 209.85 (d, $^2J_{\text{P-C}} = 25.4$ Hz, 1C, *trans*-CO); ^1H NMR (CDCl_3 , 400 MHz): δ 2.03 (s, 6H, C- CH_3), 3.70 (s, 6H, O- CH_3), 4.19 (d, $^2J_{\text{P-H}} = 3.6$ Hz, 2H, PCH), 6.29 (s, 2H, C=CH), 7.00-7.04 (m, 2H, Ar-H), 7.12-7.15 (m, 3H, Ar-H)

HRMS m/z : 562.0096 (calcd. for $\text{C}_{25}\text{H}_{21}\text{O}_7\text{PMo}$: 562.0079)

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4

From Phospholes To Primary Phosphines

Previously, we have described the formation of 7-phosphanorbornene complexes from phosphole complexes and *p*-benzoquinone. The major drawback of this route is the long reaction time required for the [4+2] cycloaddition. *N*-phenylmaleimide appeared to be an ideal replacement due to their structural similarities and higher reactivity. Unexpectedly, the metalation under identical experimental conditions gave a totally unexpected outcome, forming a dianionic phosphide *via* collapse of the phosphorus bridge. DFT studies revealed that this process takes place through a dianionic intermediate. Access to these highly reactive species have allowed for the formation of primary phosphine complexes and various phosphorus heterocycle complexes.

4.1 Introduction

The generation of terminal phosphinidene complexes has largely been performed from 7-phosphanorbornadiene complexes generated from the [4+2] cycloaddition between phosphole complexes and DMAD.¹ The tedious purification to remove excess DMAD is a huge drawback due to the ability for DMAD, a polar liquid, to affect the chromatographic isolation over silica gel. In the previous chapter, we have seen how the usage of *p*-benzoquinone as a dienophile allowed for the formation of these strained compounds after treatment with LDA. The fact that the 7-phosphanorbornene complexes are purified by a simple recrystallization is a huge draw towards its widespread use.

Success of this protocol relies on two key factors, both dependent on the presence of both the carbonyl functionalities. Firstly, the electron withdrawing ability drastically reduces the electron density around the carbon-carbon double bond, reducing the energetic requirement for the [4+2] cycloaddition to take place. Secondly, the two protons at the ring junction formed between the phosphole ring and *p*-benzoquinone rings are α -protons and hence, are easily removed due to their low pKa.

The structural similarities between *p*-benzoquinone and *N*-phenylmaleimide prompted us to explore the use of *N*-phenylmaleimide as a building block for the synthesis of 7-phosphanorbornene complexes, and their subsequent transformation into 7-phosphanorbornadiene complexes, due to its ease of use; *p*-benzoquinone needs to be purified by sublimation, recrystallization or column chromatography to remove quinhydrone and subsequently kept in the fridge. Furthermore, *p*-benzoquinone is more toxic due to its ability to sublime at room temperature and pressure.² In addition, *N*-phenylmaleimide is more reactive and reacts at a much faster rate, potentially providing a more efficient route than when *p*-benzoquinone (60 hours, 80 °C) is used as a dienophile.

In this chapter, we highlight our efforts at exploring the chemistry of cycloadducts formed from the [4+2] cycloaddition of phosphole complexes and *N*-phenylmaleimide.

4.2 Results and Discussion

Scheme 4.1 Cycloaddition Between 1-Phenylphosphole Tungsten(0) Complex and *N*-Phenylmaleimide

Our work was performed within the coordination sphere of tungsten for increased stability and ease of purification. We started with 3,4-dimethyl-1-phenylphosphole pentacarbonyltungsten(o) **24** and reacted it with *N*-phenylmaleimide in toluene at 80 °C. Monitoring of reaction progress by $^{31}\text{P}\{^1\text{H}\}$ NMR revealed that the reaction was complete in 16 hours.

7-Phenyl-7-phosphanorbornene tungsten(o) complex **59** was also characterised by X-ray crystal structure analysis. As expected, the [4+2] cycloaddition takes place on the side of the phosphole without the huge steric bulk imposed by the tungsten(o) complexing group. The cycloaddition also has an endo stereochemistry at the ring junction.

Figure 4.1 X-ray Crystal Structure of 7-Phenyl-7-Phosphanorbornene Tungsten(0) Complex **59**. Main Distances (Å) and Angles (°): P1-W1 2.4796(5), P1-C17 1.861(2), P1-C12 1.859(2), C18-C19 1.541(3), C19-C20 1.513(3), C20-O7 1.205(2); C7-P1-C12 80.93(9)

With a potential precursor successfully synthesized, we treated 7-phenyl-7-phosphanorbornene tungsten(o) complex **59** with an excess of LDA in an effort to remove the two acidic α -protons. A crude $^3\text{P}\{^1\text{H}\}$ NMR revealed the disappearance of **59**, but no new signal was observed. Upon hydrolysis, performed through the addition of water, a new signal at -86.38 ppm was observed. When another NMR spectrum was acquired without the application of broadband proton decoupling, the signal splits into a triplet, revealing the product to be phenylphosphine pentacarbonyltungsten(o) **60**.

Scheme 4.2 Metalation and Hydrolysis of 7-Phenyl-7-Phosphanorbornene Tungsten(0) Complex

The collapse of the phosphorus bridge of **59** upon metalation by an excess of LDA was totally unexpected. In order to gain some insights into the mechanism of the reaction, we performed a theoretical computation of both the monoanion and dianion of the methyl analogue of **59** at the B3LYP/6-31G(d)-LanL2DZ(W) level.³ The anions were generated by removal of the required number of α -protons at the ring junction. The optimised structure of the monoanion is shown below in Figure 4.2.

Figure 4.2 Computed Structure of Monoanion. Main Distances (Å) and Angles (°): P32-C7 1.898, P32-C12 1.881, C13-C14 1.530, C13-C17 1.404, C17-O31 1.237, C7-C14 1.568, C14-C16 1.529, C16-O30 1.228; C7-P31-C12 80.17

The bicyclic structure of the monoanion is retained. Delocalization of the carbanion at C13 is observed; the C13-C17 bond length (1.404 Å) is shortened as compared to the C14-C16 bond length (1.529 Å). In addition, the C17-O31 bond length (1.237 Å) is elongated when compared against the C16-O30 bond length (1.228 Å).

The situation is immensely different with the dianion. Its structure is seen below in Figure 4.3.

Figure 4.3 Computed Structure of Dianion. Main Distance (Å): P47-C10 2.007

The bicyclic structure has been destroyed. One of the former bridgehead phosphorus-carbon bonds (P47-C22) has broken and the other (P47-C10) is lengthened at 2.007 Å. It is evident that the reaction has to proceed through a dianionic intermediate. With this key point established, the following mechanism can be proposed.

Scheme 4.3 Proposed Mechanism For Generation of Dianionic Phosphide Tungsten(0) Complex

The cleavage of the phosphorus-carbon bond in the dianion in its conversion into **62** is driven by attainment of aromaticity in isoindoline-dione **61** and facilitated by the weakness of the long phosphorus-carbon bond. In addition, the negative charge at phosphorus is delocalised on to the complexing group; the NBO charge at P in the dianion is +0.44.

The molecular structure of aromatic by-product **61** was also confirmed by X-ray single crystal analysis.

Figure 4.4 X-ray Crystal Structure of Isoindoline-Dione **61**

This reaction pathway came as a huge surprise to us. In the previous chapter, we have reported the metalation of 7-phosphanorbornene complexes derived from *p*-benzoquinone. That reaction pathway relied on the presence of two carbonyl functionalities that allow for easy deprotonation of both α -protons for aromatization of the ring, producing the 7-phosphanorbornadiene complex framework. The electron withdrawing carbonyl moieties also allow for delocalization of the negative charge. 7-phosphanorbornene complexes derived from *N*-phenylmaleimide share the same major features, but instead of retaining the bicyclic structure with the negative charges on the electronegative oxygen atoms, the bridgehead was cleaved with destruction of the bicyclic framework, with the negative charges on the phosphorus atom. The difference in reaction patterns can be rationalised by aromaticity of the ring. With *p*-benzoquinone, the resultant benzene derivative is highly aromatic, favouring the retention of the cyclic structure. On the other hand, with *N*-phenylmaleimide, the eventual pyrrole derivative is less aromatic, and elimination of the phosphorus bridge takes place.

With **62**, we were granted access to a plethora of alkylated derivatives. With methyl iodide as an alkylating agent, tertiary phosphine complex **63** was obtained in 75% yield.

Scheme 4.4 Metalation and Methylation of 7-Phenyl-7-Phosphanorbornene Tungsten(0) Complex

The successful alkylation of **62** led us to consider whether phosphorus heterocycles could be synthesized by this protocol. Our initial attempts with 1,2-diiodoethane were unsuccessful. We wondered if the large atomic radii of the iodine atoms were hindering the nucleophilic substitution. We decided to utilise ethane-1,2-diyl dimesylate as an electrophile, in a similar vein to Bosnich's synthesis of Chiraphos.⁴ Gratifyingly, the corresponding phosphirane tungsten(o) complex was formed in 30% yield.

Scheme 4.5 Synthesis of 1-Phenylphosphirane Tungsten(0) Complex

The reaction appeared to be quite general, forming saturated heterocycles with the corresponding mesylated diols in low to modest yields.

Scheme 4.6 Synthesis of Phosphorus Heterocycle Complexes of Various Ring Sizes

In order to check the generality of this reaction, we prepared the methyl analogue by the same procedure, starting from 1,3,4-trimethylphosphole pentacarbonyltungsten(o) **33**.

Scheme 4.7 Synthesis of 7-Methyl-7-Phosphanorbornene Tungsten(0) Complex

The molecular structure of **68** was confirmed by X-ray crystallography.

Figure 4.5 X-ray Crystal Structure of 7-Phenyl-7-Phosphanorbornene Tungsten(0) Complex **68**. Main Distances (Å) and Angles (°): P1-W1 2.5257(15), P1-C7 1.865(6), P1-C12 1.854(6), C13-C14 1.528(8), C14-C15 1.517(9), C15-O6 1.198(8); C7-P1-C12 80.8(3)

Similar to **59**, the phosphorus bridge collapsed after metalation with excess LDA. Protonation of the corresponding dianion with water gave the primary phosphine tungsten(o) complex **69** as a colourless oil.

Scheme 4.8 Metalation and Hydrolysis of 7-Methyl-7-Phosphanorbornene Tungsten(0) Complex

We next wondered whether this protocol would tolerate a halogen functionality on the scaffold. We turned our attention to the β -chloroethylphosphole complex **70**. Intramolecular cyclization of the

phosphide complex should allow for the formation of phosphirane complexes.

The β -chloroethylphosphole tungsten(o) complex **70** was synthesized by treatment of phospholide complex **15** with 1,2-dichloroethane.

Scheme 4.9 Synthesis of 1-(β -Chloroethyl)phosphole Tungsten(0) Complex

Reacting phosphole complex **70** under established reaction conditions gave 7-(β -chloroethyl)-7-phosphanorbornene complex **71**.

Scheme 4.10 [4+2] Cycloaddition of 1-(β -Chloroethyl)phosphole Tungsten(0) Complex and *N*-Phenylmaleimide

Treatment of 7-phosphanorbornene complex **71** with an excess of LDA, followed by methylation with methyl iodide gave methylphosphirane tungsten(o) complex **72**. The chemistry of the parent phosphiranide complex has been described in a prior publication by Mathey and co-workers.⁵

Scheme 4.11 Synthesis of 1-Methylphosphirane Tungsten(0) Complex

We wanted to check if this protocol was compatible with other heterocycles. We prepared a phosphole complex derived from 2,3-benzofuran. Treatment of cyanophosphole **73** with lithium benzofuran-2-ide, followed by complexation gave phosphole tungsten(o) complex **74**.

Scheme 4.12 Synthesis of 1-(Benzofuran-2-yl)phosphole Tungsten(0) Complex

Reacting 1-(benzofuran-2-yl)phosphole tungsten(o) complex **74** with *N*-phenylmaleimide at 80 °C gave 7-(benzofuran-2-yl)-7-phosphanorbornene pentacarbonyltungsten(o) complex **75**.

Scheme 4.13 [4+2] Cycloaddition of 1-(Benzofuran)phosphole Tungsten(0) Complex and *N*-Phenylmaleimide

In parallel to what was done with the other 7-phosphanorbornene complexes, **75** was metalated with LDA, followed by protonation by water to yield the primary phosphine complex **76**.

Scheme 4.14 Cleavage of Phosphorus Bridge and Hydrolysis of Phosphide Tungsten(0) Complex

Primary phosphine complex **76** was also characterised by X-ray crystallographic analysis.

Figure 4.6 X-ray Crystal Structure of (Benzofuran-2-yl)phosphine Tungsten(0) Complex **76**. Main Distances (Å) and Angles (°): P1-W1 2.4705(13), P1-C6 1.792(5), C6-O6 1.389(5), C6-C7 1.349(7); C6-P1-W1 119.98(16)

We have observed that this unexpected cleavage of the phosphorus bridge is facilitated by delocalization of the first negative charge at phosphorus on to the pentacarbonyltungsten(o) complexing group. This delocalization allows for a second deprotonation, cleaving the second phosphorus-carbon bond. We wondered if it was possible to use a different electron withdrawing group. We performed the reactions with a 7-phosphanorbornene sulfide **77**.

Phosphine sulfide **77** is synthesized in an analogous manner from phosphole sulfide **45** and *N*-phenylmaleimide.

Scheme 4.15 Synthesis of 7-Phenyl-7-Phosphanorbornene Sulfide

Metalation with LDA, followed by methylation with methyl iodide gave phosphine sulfide **78** in 39% yield.

Scheme 4.16 Metalation and Methylation of 7-Phenyl-7-Phosphanorbornene Sulfide

With the chemistry of the phosphorus dianion complexes established. One last point remains to be answered; can the dianion **62** be isolated and characterised? Starting from **59**, we collapsed the bicyclic scaffold with LDA in the presence of 12-crown-4 in an attempt to stabilise the system. In the $^{31}\text{P}\{^1\text{H}\}$ NMR, we observed a signal at -128.77 ppm with a phosphorus-tungsten coupling constant of 76.1 Hz. However, we were unable to isolate this highly reactive species for further characterization and thus, its identity cannot be established with complete certainty.

Scheme 4.17 Generation of Dianionic Phosphide Tungsten(0) Complex In The Presence of 12-Crown-4

4.3 Conclusion

We have established a protocol for the conversion of phosphole complexes into the corresponding primary phosphine complexes. The dianionic

intermediate can be intercepted with various electrophiles for the synthesis of phosphine complexes or phosphorus heterocycles. This cleavage of the phosphorus bridgehead is mediated by delocalization of the negative charge at phosphorus on to the complexing group. The reaction also works with 7-phosphanorbornene sulfides, though with modest yields. This conversion of phosphole complexes to primary phosphine complexes can be viewed as the reverse of the addition of primary phosphines on to 1,3-butadiynes, forming phospholes, as first reported by Märkl⁶ and subsequently expanded by other groups.⁷ This route to primary phosphine complexes is a valuable addition to the stable of protocols for the synthesis of these extremely air-sensitive compounds, avoiding the use of phosphine gas, elemental phosphorus or tedious synthetic manipulations.⁸

4.4 Experimental Details

4.4.1 General Considerations

All reactions with air- or moisture-sensitive manipulations were carried out under positive pressure of nitrogen using standard Schlenk techniques. Tetrahydrofuran (THF) was distilled from sodium-benzophenone and toluene was distilled from sodium. All other solvents were used as received. Column chromatography was performed on Silica Gel (40-63 microns). NMR spectra were recorded on a Bruker Avance 500 spectrometer (500 MHz for ¹H, 125 MHz for ¹³C, 202 MHz for ³¹P), Bruker Avance 400 spectrometer (400 MHz for ¹H, 100 MHz for ¹³C, 162 MHz for ³¹P) or Bruker Avance 300 spectrometer (300 MHz for ¹H, 75 MHz for ¹³C, 121 MHz for ³¹P). Chemical shifts are reported in δ (ppm), referenced to the residual solvent resonance of d1-chloroform for ¹H NMR (δ = 7.26) and ¹³C NMR (δ =

77.00). ^{31}P chemical shifts are referenced to an external standard of 85% H_3PO_4 in H_2O ($\delta = 0.00$) and are uncorrected. Multiplicities are given as: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), m (multiplet). The number of protons (n) for a given resonance are given by nH and coupling constants are given as a J value in Hz. Mass spectra were recorded on a JEOL AccuTOF-DART HRMS.

4.4.2 Experimental Procedures

59

5,6-Dimethyl-2,8-diphenyl-3a,4,7,7a-tetrahydro-1*H*-4,7-phosphanoisoindole-1,3(2*H*)-dione pentacarbonyltungsten(o) (**59**)

24 (2.0484 g, 4.0 mmol) and *N*-phenylmaleimide (2.0780 g, 12.0 mmol) were dissolved in toluene (20 mL) and the mixture was heated at 80 °C for 16 hours. After cooling to room temperature, hexane was added to precipitate the target compound. The solids were filtered and washed with diethyl ether and dried under reduced pressure yielding a white solid (2.2515 g, 82 % yield)

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ 77.83 (s, $^1J_{\text{P-W}} = 241$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 15.60 (d, $^3J_{\text{P-C}} = 2.8$ Hz, 2C, $-\text{CH}_3$), 46.85 (d, $^2J_{\text{P-C}} = 5.1$ Hz, 2C, $\text{O}=\text{C}-\text{C}$), 51.39 (d, $^1J_{\text{P-C}} = 23.7$ Hz, 2C, $\text{P}-\text{CH}$), 126.32 (s, 2C, Ar-C), 127.36 (d, $^2J_{\text{P-C}} = 9.4$ Hz, 2C, Ar-C), 128.90 (s, 1C, Ar-C), 129.30 (s, 2C, Ar-C), 129.59 (d, $^3J_{\text{P-C}} = 7.4$ Hz, 2C, Ar-C), 130.14 (s, 1C, Ar-C), 131.47 (s, 1C, Ar-C),

134.16 (d, $^3J_{P-C} = 12.3$ Hz, 2C, C=C), 139.45 (d, $^1J_{P-C} = 14.1$ Hz, 1C, Ar-C), 175.08 (d, $^3J_{P-C} = 7.4$ Hz, 2C, N-C=O), 195.60 (d, $^2J_{P-C} = 7.0$ Hz, 4C, *cis*-CO), 198.06 (d, $^2J_{P-C} = 25.8$ Hz, 1C, *trans*-CO); 1H NMR (400 MHz, $CDCl_3$): δ 1.94 (d, $^4J_{P-H} = 1.6$ Hz, 6H, $-CH_3$), 3.59 (m, 2H, C=C-CH), 3.70-3.71 (m, 2H, O=C-CH), 7.03-7.05 (m, 2H, Ar-H), 7.30-7.52 (m, 8H, Ar-H)

HRMS m/z : 685.0510 (calcd. for $C_{27}H_{20}NO_7P^{184}W$: 685.0487)

60

Phenylphosphine pentacarbonyltungsten(o) (**60**)

59 (0.0685 g, 0.1 mmol) was dissolved in THF (1 mL) and LDA (0.4 mmol) in THF (1 mL) was added dropwise at 0 °C. The mixture was stirred at room temperature for 10 mins. After which, water (0.2 mL) was added and stirred for 1 hour. After removal of solvent under reduced pressure, the crude mixture was dissolved in toluene and chromatographed over silica gel at -10 °C with hexane, yielding a colourless oil. (0.0258 g, 60 %)

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ -86.38 (s, $^1J_{P-W} = 222$ Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ -86.38 (tt, $^1J_{P-H} = 340$ Hz, $^3J_{P-H} = 12.4$ Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 125.11 (d, $^1J_{P-C} = 47.0$ Hz, 1C, Ar-C), 129.22 (d, $^3J_{P-C} = 10.3$ Hz, 2C, Ar-C), 130.76 (d, $^4J_{P-C} = 2.0$ Hz, 1C, Ar-C), 132.84 (d, $^2J_{P-C} = 11.3$ Hz, 2C, Ar-C), 195.39 (d, $^2J_{P-C} = 6.7$ Hz, 4C, *cis*-CO), 198.19 (d, $^2J_{P-C} = 22.4$ Hz, 1C, *trans*-CO); 1H NMR (400 MHz, $CDCl_3$): δ 5.79 (d, $^1J_{P-H} = 340$ Hz, 2H, $-PH_2$), 7.46-7.61 (m, 5H, Ar-H)

HRMS m/z : 433.9540 (calcd. for $C_{27}H_{20}NO_5P^{184}W$: 433.9541)

615,6-Dimethyl-2-phenylisoindoline-1,3-dione (**61**)

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 20.56 (s, 2C, $-\text{CH}_3$), 124.58 (s, 2C, Ar-C), 126.49 (s, 2C, Ar-C), 127.77 (s, 2C, Ar-C), 128.95 (s, 2C, Ar-C), 129.71 (s, 2C, Ar-C), 131.92 (s, 1C, Ar-C), 144.11 (s, 1C, Ar-C), 167.54 (s, 2C, N-C=O); ^1H NMR (400 MHz, CDCl_3): δ 2.43 (s, 6H, $-\text{CH}_3$), 7.36-7.51 (m, 5H, Ar-H), 7.69 (s, 2H, Ar-H)

HRMS m/z : 251.0951 (calcd. for $\text{C}_{16}\text{H}_{13}\text{NO}_2$: 251.0946)

63Dimethylphenylphosphine pentacarbonyltungsten(o) (**63**)

59 (0.0685 g, 0.1 mmol) was dissolved in THF (1 mL) and LDA (0.4 mmol) in THF (1 mL) was added dropwise at 0 °C. The mixture was stirred at room temperature for 10 mins. After which, methyl iodide (0.19 mL, 3 mmol) was added and stirred for 1 hour. After removal of solvent under reduced pressure, the crude mixture was dissolved in toluene and chromatographed over silica gel at -10 °C with hexane, yielding a colourless oil. (0.0345 g, 75 %)

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ -23.77 (s, $^1J_{\text{P-W}} = 232$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 20.23 (d, $^1J_{\text{P-C}} = 28.9$ Hz, 2C, $-\text{CH}_3$), 128.72 (d, $^2J_{\text{P-C}} = 3.9$ Hz, 2C, Ar-C), 128.82 (d, $^3J_{\text{P-C}} = 2.7$ Hz, 2C, Ar-C), 129.81 (s, 1C, Ar-C), 138.36 (d, $^1J_{\text{P-C}} = 41.2$ Hz, 1C, Ar-C), 175.08 (d, $^3J_{\text{P-C}} = 7.4$ Hz, 2C, N-C=O), 197.00 (d, $^2J_{\text{P-C}} = 6.9$ Hz, 4C, *cis*-CO), 199.91 (d, $^2J_{\text{P-C}} = 19.6$ Hz, 1C, *trans*-CO); ^1H NMR (400 MHz, CDCl_3): δ 1.98 (d, $^2J_{\text{P-H}} = 7.6$ Hz, 6H, $-\text{CH}_3$), 7.40-7.53 (m, 5H, Ar-H)

HRMS m/z : 461.9868 (calcd. for $\text{C}_{13}\text{H}_{11}\text{O}_5\text{P}^{184}\text{W}$: 461.9854)

64

1-Phenylphosphirane pentacarbonyltungsten(o) (**64**)

59 (0.0685 g, 0.1 mmol) was dissolved in THF (1 mL). LDA (0.4 mmol) in THF (1 mL) was added dropwise at 0 °C, and the mixture was stirred at room temperature for 10 min. Ethane-1,2-diyl dimesylate (0.0205 g, 0.11 mmol) was then added and stirred for 18 h. After removal of solvent under reduced pressure, the crude mixture was dissolved in toluene and purified over silica gel at -10 °C with hexane, yielding a colourless oil (0.0118 g, 30 %).

$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CD_2Cl_2): δ -187.52 (s, $^1J_{\text{P-W}} = 257$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_2Cl_2): δ 11.30 (d, $^1J_{\text{P-C}} = 12.2$ Hz, 2C, P- CH_2), 129.21 (d, $^3J_{\text{P-C}} = 10.5$ Hz, 2C, Ar-C), 130.78 (d, $^4J_{\text{P-C}} = 2.3$ Hz, 1C, Ar-C), 131.84 (d, $^2J_{\text{P-C}} = 13.2$ Hz, 2C, Ar-C), 134.40 (d, $^1J_{\text{P-C}} = 30.1$ Hz, 1C, Ar-C), 197.04 (d, $^2J_{\text{P-C}} = 8.3$ Hz, 4C, *cis*-CO), 198.57 (d, $^2J_{\text{P-C}} = 30.1$ Hz, 1C, *trans*-CO); ^1H NMR (300 MHz,

CD_2Cl_2): δ 1.42-1.48 (m, 2H, $-\text{PCH}_2$), 1.73-1.81 (m, 2H, $-\text{PCH}_2$), 7.40-7.43 (m, 3H, Ar- H), 7.48-7.56 (m, 2H, Ar- H)

HRMS m/z : 459.9710 (calcd. for $\text{C}_{13}\text{H}_9\text{O}_5\text{P}^{184}\text{W}$: 459.9697)

1-Phenylphosphetane pentacarbonyltungsten(o) (**65**)

59 (0.0685 g, 0.1 mmol) was dissolved in THF (1 mL). LDA (0.4 mmol) in THF (1 mL) was added dropwise at 0 °C, and the mixture was stirred at room temperature for 10 min. Propane-1,3-diyl dimesylate (0.0220 g, 0.11 mmol) was then added and stirred for 18 h. After removal of solvent under reduced pressure, the crude mixture was dissolved in toluene and purified over silica gel at -10 °C with hexane, yielding a colourless oil (0.0090 g, 19 %).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ 29.78 (s, $^1J_{\text{P-W}} = 222$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 23.38 (d, $^2J_{\text{P-C}} = 17.3$ Hz, 2C, P- $\text{CH}_2\text{-CH}_2$), 28.12 (d, $^1J_{\text{P-C}} = 35.2$ Hz, 2C, P- $\text{CH}_2\text{-CH}_2$), 128.48 (d, $^2J_{\text{P-C}} = 10.7$ Hz, 2C, Ar- C), 128.82 (d, $^3J_{\text{P-C}} = 9.1$ Hz, 2C, Ar- C), 129.59 (d, $^4J_{\text{P-C}} = 1.9$ Hz, 1C, Ar- C), 139.40 (d, $^1J_{\text{P-C}} = 27.1$ Hz, 1C, Ar- C), 196.59 (d, $^2J_{\text{P-C}} = 7.1$ Hz, 4C, *cis*-CO), 200.16 (d, $^2J_{\text{P-C}} = 21.1$ Hz, 1C, *trans*-CO); ^1H NMR (400 MHz, CDCl_3): δ 2.60-2.78 (m, 6H, $-\text{CH}_2-$), 7.42-7.53 (m, 5H, Ar- H)

HRMS m/z : 473.9851 (calcd. for $\text{C}_{14}\text{H}_{11}\text{O}_5\text{P}^{184}\text{W}$: 473.9854)

66

1-Phenylphospholane pentacarbonyltungsten(o) (**66**)

59 (0.0685 g, 0.1 mmol) was dissolved in THF (1 mL). LDA (0.4 mmol) in THF (1 mL) was added dropwise at 0 °C, and the mixture was stirred at room temperature for 10 min. Butane-1,4-diyl dimesylate (0.0235 g, 0.11 mmol) was then added and stirred for 18 h. After removal of solvent under reduced pressure, the crude mixture was dissolved in toluene and purified over silica gel at -10 °C with hexane, yielding a colourless oil (0.0155 g, 32 %).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ 3.92 (s, $^1J_{\text{P-W}} = 227$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 27.4 (s, 2C, P- CH_2CH_2 -), 32.86 (d, $^1J_{\text{P-C}} = 26.7$ Hz, 2C, P- CH_2 -), 128.81 (d, $^3J_{\text{P-C}} = 8.9$ Hz, 2C, Ar-C), 128.92 (d, $^2J_{\text{P-C}} = 10.0$ Hz, 2C, Ar-C), 129.34 (d, $^4J_{\text{P-C}} = 1.8$ Hz, 1C, Ar-C), 138.46 (d, $^1J_{\text{P-C}} = 33.2$ Hz, 1C, Ar-C), 196.95 (d, $^2J_{\text{P-C}} = 7.1$ Hz, 4C, *cis*-CO), 200.10 (d, $^2J_{\text{P-C}} = 20.3$ Hz, 1C, *trans*-CO); ^1H NMR (400 MHz, CDCl_3): δ 1.79-1.97 (m, 4H, - CH_2), 2.26-2.33 (m, 2H, - CH_2), 2.55-2.60 (m, 2H, - CH_2), 7.35-7.46 (m, 5H, Ar-*H*)

HRMS m/z : 488.0007 (calcd. for $\text{C}_{15}\text{H}_{13}\text{O}_5\text{P}^{184}\text{W}$: 488.0010)

67

1-Phenylphosphinane pentacarbonyltungsten(o) (**67**)

59 (0.0685 g, 0.1 mmol) was dissolved in THF (1 mL). LDA (0.4 mmol) in THF (1 mL) was added dropwise at 0 °C, and the mixture was stirred at room temperature for 10 min. Pentane-1,5-diyl dimesylate (0.0251 g, 0.11 mmol) was then added and stirred for 18 h. After removal of solvent under reduced pressure, the crude mixture was dissolved in toluene and purified over silica gel at -10 °C with hexane, yielding a colourless oil (0.0162 g, 32 %).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3): δ -15.24 (s, $^1J_{\text{P-W}} = 230$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 22.39 (d, $^2J_{\text{P-C}} = 6.0$ Hz, 2C, P- CH_2CH_2 -), 26.54 (d, $^3J_{\text{P-C}} = 3.3$ Hz, 1C, P- $\text{CH}_2\text{CH}_2\text{CH}_2$ -), 28.82 (d, $^1J_{\text{P-C}} = 25.4$ Hz, 2C, P- CH_2 -), 128.70 (d, $^4J_{\text{P-C}} = 8.63$ Hz, 1C, Ar-C), 129.02 (d, $^3J_{\text{P-C}} = 8.75$ Hz, 2C, Ar-C), 129.18 (s, 1C, Ar-C), 135.83 (d, $^1J_{\text{P-C}} = 37.9$ Hz, 1C, Ar-C), 197.03 (d, $^2J_{\text{P-C}} = 7.0$ Hz, 4C, *cis*-CO), 200.2 (d, $^2J_{\text{P-C}} = 19.3$ Hz, 1C, *trans*-CO); ^1H NMR (400 MHz, CDCl_3): δ 1.49-1.68 (m, 4H, - CH_2), 1.80-1.89 (m, 2H, - CH_2), 2.15-2.21 (m, 2H, - CH_2), 2.49-2.53 (m, 2H, - CH_2), 7.35-7.50 (m, 5H, Ar-H)

HRMS m/z : 502.0165 (calcd. for $\text{C}_{16}\text{H}_{15}\text{O}_5\text{P}^{184}\text{W}$: 502.0167)

68

5,6,8-Trimethyl-2-phenyl-3a,4,7,7a-tetrahydro-1*H*-4,7-phosphanoisoindole-1,3(2*H*)-dione pentacarbonyltungsten(o) (**68**)

33 (0.4500 g, 1.0 mmol) and *N*-phenylmaleimide (0.5195 g, 3.0 mmol) were dissolved in toluene (5 mL) and the mixture was heated at 80 °C for 16 hours. After cooling to room temperature, hexane was added to precipitate the target compound. The solids were filtered and washed with diethyl ether and dried under reduced pressure yielding an off-white solid (0.4657 g, 75 % yield)

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ 63.71 (s, $^1\text{J}_{\text{P-W}} = 241$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 15.51 (d, $^3\text{J}_{\text{P-C}} = 2.9$ Hz, 2C, - CH_3), 20.12 (d, $^1\text{J}_{\text{P-C}} = 2.7$ Hz, 1C, P- CH_3), 46.48 (d, $^2\text{J}_{\text{P-C}} = 4.8$ Hz, 2C, O=C-C), 51.36 (d, $^1\text{J}_{\text{P-C}} = 24.0$ Hz, 2C, P-CH), 126.41 (s, 2C, Ar-C), 129.02 (s, 1C, Ar-C), 129.39 (s, 2C, Ar-C), 131.51 (s, 1C, Ar-C), 135.28 (d, $^2\text{J}_{\text{P-C}} = 12.2$ Hz, 2C, C=C), 174.82 (d, $^3\text{J}_{\text{P-C}} = 7.0$ Hz, 2C, N-C=O), 195.88 (d, $^2\text{J}_{\text{P-C}} = 6.7$ Hz, 4C, *cis*-CO), 197.65 (d, $^2\text{J}_{\text{P-C}} = 28.3$ Hz, 1C, *trans*-CO); ^1H NMR (400 MHz, CDCl_3): δ 1.79 (d, $^2\text{J}_{\text{P-H}} = 5.6$ Hz, 3H, P- CH_3), 1.84 (d, $^4\text{J}_{\text{P-H}} = 1.6$ Hz, 6H, C- CH_3), 3.25-3.27 (m, 2H, C=C-CH), 3.81-3.82 (m, 2H, O=C-CH), 7.08-7.10 (m, 2H, Ar-H), 7.41-7.49 (m, 3H, Ar-H)

HRMS m/z : 623.0330 (calcd. for $\text{C}_{22}\text{H}_{18}\text{NO}_7\text{P}^{184}\text{W}$: 623.0330)

69

Methylphosphine pentacarbonyltungsten(o) (**69**)

68 (0.1246 g, 0.2 mmol) was dissolved in THF (1.5 mL) and LDA (0.8 mmol) in THF (1 mL) was added dropwise at 0 °C. The mixture was stirred at room temperature for 10 mins. After which, water (0.5 mL) was added and stirred for 1 hour. After removal of solvent under reduced pressure, the crude mixture was dissolved in toluene and chromatographed over silica gel at -10 °C with hexane, yielding a colourless oil. (0.0230 g, 62 %)

$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CDCl_3): δ -120.14 (s, $^1J_{\text{P-W}} = 220$ Hz); ^{31}P NMR (121 MHz, CDCl_3): δ -120.14 (tq, $^1J_{\text{P-H}} = 335$ Hz, $^2J_{\text{P-H}} = 8.9$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 4.88 (d, $^1J_{\text{P-C}} = 31.4$ Hz, 1C, P- CH_3), 195.51 (d, $^2J_{\text{P-C}} = 7.1$ Hz, 4C, *cis*-CO), 198.34 (d, $^2J_{\text{P-C}} = 22.1$ Hz, 1C, *trans*-CO); ^1H NMR (300 MHz, CDCl_3): δ 1.69-1.76 (m, 3H, P- CH_3), 4.65 (dq, $^1J_{\text{P-H}} = 335$ Hz, $^3J_{\text{H-H}} = 6.9$ Hz, 2H, P- CH_3)

HRMS m/z : 371.9397 (calcd. for $\text{C}_{27}\text{H}_{20}\text{NO}_5\text{P}^{184}\text{W}$: 371.9384)

70

1-(2-Chloroethyl)-3,4-dimethylphosphole pentacarbonyltungsten(o) (**70**)

A solution of **15** (from 5.5 mL of **17**) was added dropwise to a flask of 1,2-dichloroethane (10 mL). After stirring for 1 hour, the solution was

concentrated and chromatographed over silica gel at -10 °C, yielding the phosphole complex as a yellow solid.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ 1.03 (s, $^1J_{\text{P-W}} = 216$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 17.10 (d, $^3J_{\text{P-C}} = 12.0$ Hz, 2C, -CH₃), 33.14 (d, $^1J_{\text{P-C}} = 20.0$ Hz, 1C, P-CH₂), 39.75 (d, $^2J_{\text{P-C}} = 4.0$ Hz, 1C, -CH₂Cl), 127.52 (d, $^1J_{\text{P-C}} = 41.0$ Hz, 2C, P-CH₂), 151.93 (d, $^2J_{\text{P-C}} = 8.0$ Hz, 2C, C-CH₃), 195.68 (d, $^2J_{\text{P-C}} = 7.0$ Hz, 4C, *cis*-CO), 198.68 (d, $^2J_{\text{P-C}} = 18.0$ Hz, 1C, *trans*-CO); ^1H NMR (400 MHz, CDCl_3): δ 2.17 (s, 6H, -CH₃), 2.47-2.53 (m, 2H, P-CH₂), 3.37-3.43 (m, 2H, -CH₂Cl), 6.30 (d, $^2J_{\text{P-H}} = 37.2$ Hz, 2H, PCH)

8-(2-Chloroethyl)-5,6-dimethyl-2-phenyl-3a,4,7,7a-tetrahydro-1H-4,7-phosphanoisindole-1,3(2H)-dione pentacarbonyltungsten(o) (**71**)

70 (0.4985 g, 1.0 mmol) and *N*-phenylmaleimide (0.5195 g, 3.0 mmol) were dissolved in toluene (5 mL) and the mixture was heated at 80 °C for 16 hours. After cooling to room temperature, hexane was added to precipitate the target compound. The solids were filtered and washed with diethyl ether and dried under reduced pressure yielding a pale-yellow solid (0.4692 g, 70 % yield).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ 73.34 (s, $^1J_{\text{P-W}} = 246$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 15.65 (s, 2C, -CH₃), 35.73 (s, 1C, -CH₂-), 40.55 (s, 1C, -CH₂-), 46.64 (s, 2C, O=C-C), 51.80 (d, $^1J_{\text{P-C}} = 23.0$ Hz, 2C, P-CH), 126.42 (s,

2C, Ar-C), 129.08 (s, 1C, Ar-C), 129.43 (s, 2C, Ar-C), 131.47 (s, 1C, Ar-C), 135.25 (d, $^2J_{P-C} = 12.6$ Hz, 2C, C=C), 174.67 (d, $^3J_{P-C} = 7.0$ Hz, 2C, N-C=O), 195.56 (d, $^2J_{P-C} = 6.6$ Hz, 4C, *cis*-CO), 196.55 (d, $^2J_{P-C} = 27.4$ Hz, 1C, *trans*-CO); 1H NMR (400 MHz, $CDCl_3$): δ 1.85 (d, $^4J_{P-H} = 1.6$ Hz, 6H, -CH₃), 2.41-2.44 (m, 2H, -CH₂-), 3.40-3.41 (m, 2H, C=C-CH), 3.88-3.93 (m, 4H, overlapping O=C-CH & -CH₂-), 7.07-7.09 (m, 2H, Ar-H), 7.39-7.49 (m, 8H, Ar-H)

HRMS *m/z*: 671.0099 (calcd. for C₂₃H₁₉ClO₇P¹⁸⁴W: 671.0097)

72

1-Methylphosphirane pentacarbonyltungsten(o) (**72**)

71 (0.1342 g, 0.2 mmol) was dissolved in THF (1 mL) and LDA (0.8 mmol) in THF (1 mL) was added dropwise at 0 °C. The mixture was stirred at room temperature for 10 mins. After which, methyl iodide (0.19 mL, 3 mmol) was added and stirred for 1 hour. After removal of solvent under reduced pressure, the crude mixture was dissolved in toluene and chromatographed over silica gel at -10 °C with hexane, yielding a colourless oil. (0.0066 g, 17 %)

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ -200.46 (s, $^1J_{P-W} = 254$ Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 8.68 (d, $^2J_{P-C} = 10.8$ Hz, 2C, P-CH₂-), 16.98 (d, $^1J_{P-C} = 15.8$ Hz, 1C, P-CH₃), 195.61 (d, $^2J_{P-C} = 8.2$ Hz, 4C, *cis*-CO), 197.97 (d, $^2J_{P-C} = 29.2$ Hz, 1C, *trans*-CO); 1H NMR (400 MHz, $CDCl_3$): δ 1.12-1.14 (m, 2H, -

PCH_2^-), 1.26-1.29 (m, 2H, $-\text{PCH}_2^-$), 1.38 (d, $^2J_{\text{P-H}} = 7.2$ Hz, 3H, P-CH_3).

HRMS m/z : 397.9549 (calcd. for $\text{C}_{27}\text{H}_{20}\text{NO}_5\text{P}^{184}\text{W}$: 397.9541)

1-(Benzofuran-2-yl)-3,4-dimethylphosphole pentacarbonyltungsten(o) (**74**)

To a solution of 2,3-benzofuran (0.591 g, 5 mmol) in THF (30 mL) was added $n\text{BuLi}$ (2.5 mL, 5 mmol) at 0 °C and stirred at room temperature for 1.5 hours. The resultant solution was then added to a solution of **73** (generated from 5.5 mmol of **17**) in THF (20 mL) at -78 °C, warmed to room temperature and stirred for 2 hours. Evaporation of solvent and rapid chromatography over silica with dichloromethane yielded the crude phosphole complex ($^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ -27.29 (s); HRMS m/z : 228.0693 (calcd. for $\text{C}_{14}\text{H}_{13}\text{OP}$: 228.0704)), which was used without further purification. To the phosphole was added a freshly made solution of $\text{W}(\text{CO})_5\text{MeCN}$ (1.45 g, 4.0 mmol). The mixture was stirred for 12 hours at room temperature, concentrated and chromatographed over silica gel with hexane at -10 °C, yielding a yellow solid. (0.3893 g, 18%)

$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CDCl_3): δ -7.04 (s, $^1J_{\text{P-W}} = 218$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 17.38 (d, $^3J_{\text{P-C}} = 12.0$ Hz, 2C, $-\text{CH}_3$), 111.62 (s, 1C, Ar-C), 115.77 (d, $^2J_{\text{P-C}} = 16.0$ Hz, 2C, $\text{C}=\text{C}$), 121.56 (s, 1C, Ar-C), 123.25 (s, 1C, Ar-C), 125.90 (s, 1C, Ar-C), 127.39 (d, $^1J_{\text{P-C}} = 46.2$ Hz, 2C, Ar-C), 127.45 (d, $^3J_{\text{P-C}} = 7.1$ Hz, 1C, Ar-C), 149.19 (d, $^1J_{\text{P-C}} = 50.3$ Hz, 1C, Ar-C), 152.32 (d, $^2J_{\text{P-C}} = 10.5$

Hz, 1C, Ar-C), 157.61 (d, $^3J_{P-C} = 5.3$ Hz, 1C, Ar-C), 195.64 (d, $^2J_{P-C} = 6.8$ Hz, 4C, *cis*-CO), 198.57 (d, $^2J_{P-C} = 18.8$ Hz, 1C, *trans*-CO); 1H NMR (300 MHz, $CDCl_3$): δ 2.28 (s, 6H, $-CH_3$), 6.51 (d, $^2J_{P-H} = 37.5$ Hz, 2H, $-PCH$), 7.17 (d, $^3J_{P-H} = 1.5$ Hz, 1H, $-PCCH$), 7.28-7.40 (m, 2H, ArH), 7.51-7.54 (m, 1H, Ar-H), 7.60-7.63 (m, 1H, Ar-H)

HRMS m/z : 551.9957 (calcd. for $C_{19}H_{13}O_6P^{184}W$: 551.9959)

8-(Benzofuran-2-yl)-5,6-dimethyl-2-phenyl-3a,4,7,7a-tetrahydro-1H-4,7-phosphanoisindole-1,3(2H)-dione pentacarbonyltungsten(o) (**75**)

74 (0.3022 g, 0.54 mmol) and *N*-phenylmaleimide (0.2598 g, 1.5 mmol) were dissolved in toluene (5 mL) and the mixture was heated at 80 °C for 16 hours. After cooling to room temperature, hexane was added to precipitate the target compound. The solids were filtered and washed with diethyl ether and dried under reduced pressure yielding a pale-yellow solid. (0.2715g, 68 % yield)

$^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 53.65 (s, $^1J_{P-W} = 249$ Hz); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 15.86 (d, $^3J_{P-C} = 3.0$ Hz, 2C, $-CH_3$), 47.73 (d, $^2J_{P-C} = 4.0$ Hz, 2C, O=C-C), 52.71 (d, $^1J_{P-C} = 25.0$ Hz, 2C, P-CH), 112.08 (s, 1C, Ar-C), 112.88 (d, $^2J_{P-C} = 9.9$ Hz, 1C, Ar-C), 122.35 (s, 1C, Ar-C), 124.23 (s, 1C, Ar-C), 126.70 (s, 1C, Ar-C), 127.06 (s, 2C, Ar-C), 127.22 (d, $^3J_{P-C} = 4.5$ Hz, 1C, Ar-C),

129.36 (s, 1C, Ar-C), 129.67 (s, 2C, Ar-C), 132.24 (s, 1C, Ar-C), 134.59 (d, $^2J_{P-C}$ = 13.8 Hz, 2C, C=C), 155.59 (d, $^1J_{P-C}$ = 15.0 Hz, 1C, Ar-C), 157.07 (d, $^3J_{P-C}$ = 4.0 Hz, 1C, Ar-C), 175.24 (d, $^3J_{P-C}$ = 8.0 Hz, 2C, N-C=O), 195.73 (d, $^2J_{P-C}$ = 7.0 Hz, 4C, *cis*-CO), 198.26 (d, $^2J_{P-C}$ = 28.0 Hz, 1C, *trans*-CO); 1H NMR (400 MHz, CD_2Cl_2): δ 1.95 (s, 6H, C-CH₃), 3.79-3.84 (m, 4H, Overlapping C=C-CH & O=C-CH), 7.06-7.12 (m, 3H, Ar-H), 7.31-7.49 (m, 5H, Ar-H), 7.59-7.61 (m, 1H, Ar-H), 7.66-7.68 (m, 1H, Ar-H)

HRMS m/z : 725.0443 (calcd. for $C_{29}H_{20}NO_8P^{184}W$: 725.0436)

76

Benzofuran-2-ylphosphine pentacarbonyltungsten(o) (**76**)

75 (0.0725 g, 0.1 mmol) was dissolved in THF (1.0 mL) and LDA (0.2 mmol) in THF (1 mL) was added dropwise at 0 °C. The mixture was stirred at room temperature for 10 mins. After which, water (0.1 mL) was added and stirred for 1 hour. After removal of solvent under reduced pressure, the crude mixture was dissolved in toluene and chromatographed over silica gel at -10 °C with hexane, yielding a pale yellow solid (0.0146 g, 31 %).

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ -115.24 (s, $^1J_{P-W}$ = 228 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ -115.24 (t, $^1J_{P-H}$ = 351 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 111.63 (s, 1C, Ar-C), 119.46 (d, $^2J_{P-C}$ = 20.0 Hz, 1C, Ar-C), 121.83 (s, 1C, Ar-C), 123.62 (s, 1C, Ar-C), 126.59 (s, 1C, Ar-C), 127.37 (d, $^3J_{P-C}$ = 9.0 Hz, 1C, Ar-C), 143.68 (d, $^1J_{P-C}$ = 55.0 Hz, 1C, Ar-C), 158.19 (s, 1C, Ar-C), 194.78 (d, $^2J_{P-C}$ = 7.0 Hz, 4C, *cis*-CO), 197.21 (d, $^2J_{P-C}$ = 24.0 Hz, 1C, *trans*-CO); 1H NMR (400

MHz, CDCl_3): δ 5.918 (d, $^1J_{\text{P-H}} = 351$ Hz, 2H, PH_2), 7.284-7.423 (m, 3H, Ar-*H*), 7.52-7.54 (m, 1H, Ar-*H*), 7.64-7.65 (m, 1H, Ar-*H*)

HRMS m/z : 473.9489 (calcd. for $\text{C}_{13}\text{H}_6\text{O}_6\text{P}^{184}\text{W}$: 473.9490)

5,6-Dimethyl-2,8-diphenyl-3a,4,7,7a-tetrahydro-1*H*-4,7-phosphanoisoindole-1,3(2*H*)-dione 8-sulfide (**77**)

45 (2.0484 g, 4.0 mmol) and *N*-phenylmaleimide (2.0780 g, 12.0 mmol) were dissolved in toluene (20 mL) and the mixture was heated at 80 °C for 16 hours. After cooling to room temperature, hexane was added to precipitate the target compound. The solids were filtered and washed with diethyl ether and dried under reduced pressure yielding a cream solid.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ 106.89 (s); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 15.25 (d, $^3J_{\text{P-C}} = 4.0$ Hz, 2C, $-\text{CH}_3$), 45.06 (d, $^2J_{\text{P-C}} = 18.0$ Hz, 2C, $\text{O}=\text{C}-\text{C}$), 52.17 (d, $^1J_{\text{P-C}} = 51.0$ Hz, 2C, $\text{P}-\text{CH}$), 126.45 (s, 2C, Ar-*C*), 128.86 (s, 1C, Ar-*C*), 128.97 (d, $^3J_{\text{P-C}} = 2.0$ Hz, 2C, Ar-*C*), 129.34 (s, 2C, Ar-*C*), 129.59 (d, $^2J_{\text{P-C}} = 10.0$ Hz, 2C, Ar-*C*), 130.21 (s, 1C, Ar-*C*), 131.00 (s, 1C, Ar-*C*), 131.66 (d, $^3J_{\text{P-C}} = 3.0$ Hz, 2C, $\text{C}=\text{C}$), 139.79 (d, $^1J_{\text{P-C}} = 7.0$ Hz, 1C, Ar-*C*), 175.50 (d, $^3J_{\text{P-C}} = 15.0$ Hz, 2C, $\text{N}-\text{C}=\text{O}$); ^1H NMR (400 MHz, CDCl_3): δ 1.63 (d, $^4J_{\text{P-H}} = 2.0$ Hz, 6H, $-\text{CH}_3$), 3.54-3.57 (m, 2H, $\text{C}=\text{C}-\text{CH}$), 4.31-4.32 (m, 2H, $\text{O}=\text{C}-\text{CH}$), 7.08-7.10 (m, 2H, Ar-*H*), 7.39-7.61 (m, 8H, Ar-*H*)

78Dimethylphenylphosphine sulfide (**78**)

77 (0.0393 g, 0.1 mmol) was dissolved in THF (1 mL) and LDA (0.4 mmol) in THF (1 mL) was added dropwise at 0 °C. The mixture was stirred at room temperature for 10 mins. After which, methyl iodide (0.19 mL, 3 mmol) was added and stirred for 1 hour. After removal of solvent under reduced pressure, the crude mixture was dissolved in toluene and chromatographed over silica gel at -10 °C with hexane, yielding a colourless oil (0.0131 g, 39 %).

$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CDCl_3): δ 33.27 (s); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 22.89 (d, $^1J_{\text{P-C}} = 57.0$, 2C, P- CH_3), 128.65 (d, $^2J_{\text{P-C}} = 12.0$ Hz, 2C, Ar-C), 130.0 (d, $^3J_{\text{P-C}} = 10.6$ Hz, 2C, Ar-C), 131.50 (d, $^4J_{\text{P-C}} = 2.9$ Hz, 1C, Ar-C), 133.72 (d, $^1J_{\text{P-C}} = 79.5$ Hz, 1C, Ar-C); ^1H NMR (300 MHz, CDCl_3): δ 1.98 (d, $^2J_{\text{P-H}} = 13.2$ Hz 6H, - PCH_3), 7.51-7.52 (m, 3H, Ar- H), 7.86-7.94 (m, 2H, Ar- H)

HRMS m/z : 170.0309 (calcd. for $\text{C}_8\text{H}_{11}\text{PS}$: 170.0319)

4.5 References

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5

Isomerization Of Secondary Phosphiranes Into Phosphinidene Complexes

A secondary phosphirane complex was synthesized as a potential precursor to the parent phosphinidene complex. Unexpectedly, an isomerization took place, giving a terminal phosphinidene complex that was trapped by alkenes and alkynes. The formation of terminal phosphinidene complexes with no by-products is a rare example of isomerization of a P(III) derivative into a P(I) derivative. DFT studies revealed the concerted nature of the hydrogen shift.

5.1 Introduction

The generation of electrophilic terminal phosphinidene complexes has opened many avenues to a plethora of novel organophosphorus compounds. The high synthetic value in these highly reactive, transient species lies in the range of substituents that can be used on the monovalent phosphorus moiety. Apart from ‘normal’ substituents like alkyls and aryls,¹ functional groups such as halides,² cyano,³ esters,³ alkenes,⁴ alkynes,⁵ phosphino,⁶ ferrocenyl⁷ and pentamethylcyclopentadienyl⁸ are also tolerated. Furthermore, there are molecular scaffolds that can only be synthesized with the use of terminal phosphinidene complexes. For example, the [2+1] cycloaddition of electrophilic phosphinidene complexes and alkynes remains the most general route to phosphirenes.⁹

One glowing omission from the chemical literature is the generation of the parent phosphinidene, PH. This highly reactive species has been detected in interstellar clouds¹⁰ and within the planetary atmosphere of Uranus.¹¹ The generation of the parent phosphinidene (or its metal complexes) would open pathways to a myriad of primary and secondary phosphines and their complexes, some of which can be seen in Figure 5.1.

Figure 5.1 Potential Synthetic Applications of the Parent Phosphinidene Complex

The range of possibilities available, should such a species be generated, tempted us to attempt to find a generating system. In this chapter, we report our findings regarding synthesis of a potential precursor, and its unexpected isomerization.

5.2 Results and Discussion

The generation of the parent phosphinidene complex is not a trivial matter. Chapter 1 has highlighted the various generating systems, namely the metal complexes of 7-phosphanorbornadienes,^{1a} phosphiranes,¹² phosphirenes,¹³ azaphosphirenes,¹⁴ benzophosphepines^{1c} and by salt metathesis.¹⁵ The salt metathesis route is not a viable pathway as an amino substituent is usually necessary. Benzophosphepine complexes should work, but the precursor

would be difficult, if not impossible to synthesize and isolate in a viable yield. These bicyclic structures are made from a double hydrophosphination of primary phosphine complexes on 1,2-bis(ethynyl)benzene. While phosphine pentacarbonyltungsten(o) can be synthesized,¹⁶ the presence of the last phosphorus-hydrogen bond should lead to a range of undesirable side products. At the moment, all available azaphosphirene complexes have extremely bulky substituents on the phosphorus, precluding its use. Phosphirene complexes are much too stable and indeed, only the aminophosphinidene complex has been generated at reasonable temperatures. The secondary 7-phosphanorbornadiene cannot be generated from the corresponding secondary phosphole. The initial 1*H*-phosphole **80** rapidly isomerizes to the 2*H*-phosphole **81**.¹⁷ This takes place *via* a [1,5] sigmatropic shift. This process occurs almost immediately at room temperature. 2*H*-Phospholes are extremely reactive as dienes and dienophiles and spontaneously dimerize to form a bicyclic framework with a phosphorus-phosphorus bond **82**.

Scheme 5.1 [1,5] Sigmatropic Shift of Secondary Phospholes and its Subsequent Dimerization

Complexation with pentacarbonyltungsten(o) imparts a degree of stability, but this impedes the rate minimally and dimerization still takes place, though through a different mechanism.¹⁸

The only route that appears to be viable is using phosphirane complexes as a generating system. It has been shown by Mathey and co-workers that phosphirane complexes that are annulated on a cyclohexane ring are excellent precursors.⁷ For example, ferrocenylphosphirane tungsten(o) complex **83** undergoes a [2+1] retroaddition, forming ferrocenylphosphinidene tungsten(o) complex **84**. Trapping with diphenylacetylene gives phosphirene tungsten(o) complex **85**.

Scheme 5.2 Generation of Ferrocenylphosphinidene Tungsten(0) Complex From Phosphirane Complexes

We envisaged that reduction of the chloro analogue of **83**^{2a} might give us a potential precursor to the parent species.

The synthesis starts with phospholyl tungsten(o) complex **15**. **15** was added dropwise to a THF solution of hexachloroethane, forming 1-chlorophosphole tungsten(o) complex **1**.

Scheme 5.3 Synthesis of 1-Chlorophosphole Tungsten(0) Complex

The dropwise addition of **15** to an excess of hexachloroethane is absolutely essential. If the addition is too rapid or if hexachloroethane is limiting, **15** can react with a molecule of **1**, forming phosphole tungsten(o) complex dimer **86**. It must be noted that the formation of **86** cannot be completely avoided, and is always observed in the crude $^{31}\text{P}\{^1\text{H}\}$ NMR.

Scheme 5.4 Formation of Unwanted Phosphole Tungsten(0) Complex Dimer

7-Chloro-7-phosphanorbornadiene tungsten(o) complex formed from the [4+2] cycloaddition of DMAD and 1-chlorophosphole pentacarbonyltungsten(o) **1** is unstable and decomposes under reaction conditions.¹⁹ The solution to this was to trap chlorophosphinidene complex **10** *in situ* with a trapping agent. The trapping agent of choice was cyclohexene, forming the corresponding phosphirane complex **87**.

Scheme 5.5 Generation of 1-Chlorophosphirane Tungsten(0) Complex

We treated **87** with a variety of reducing agents, some of which proved ineffective; either no reaction (sodium borohydride), partial decomposition (lithium aluminium hydride) or hydrolysis (sodium hydride, probably due to contamination by sodium hydroxide) was observed. However, tributyltin hydride proved to be an effective reducing agent, yielding the two inseparable diastereomers in a combined yield of 59%. The high field chemical shift (around -220 ppm) and large phosphorus-hydrogen coupling constant (341 Hz) is consistent with a three-membered ring with a one-bond phosphorus-hydrogen linkage.

Scheme 5.6 Reduction of P-Cl Bond To Yield a Secondary Phosphirane Tungsten(0) Complex

The major isomer was also characterised by single crystal X-ray crystallography.

Figure 5.2 X-ray Crystal Structure of Secondary Phosphirane Tungsten(0) Complex **88b**. Main Distances (Å) and Angles (°): P1-W1 2.490(2), P1-C4 1.85(4), P1-C9 1.82(4), C4-C9 1.535(17); C4-P1-C9 49.5(5)

The major product **88b** had the bulky pentacarbonyltungsten(o) complexing group projected away from the six-membered ring, the opposite of what is observed with **87**, where the major product has the complexing group over the six-membered ring.

With a potential precursor of the parent terminal phosphinidene complex in our possession, we attempted to generate and trap the transient species with diphenylacetylene. Monitoring the reaction by $^{31}\text{P}\{^1\text{H}\}$ NMR revealed that the reaction was complete after 7 hours at 110 °C, as evidenced by total disappearance of the signal corresponding to the starting phosphirane complex **87**. The reaction was extremely clean, giving a new signal at -141 ppm, consistent with the presence of a three-membered ring.⁹ However, when the NMR was reacquired without broadband proton decoupling, no significant phosphorus-hydrogen coupling was observed, suggesting that phosphirene tungsten(o) complex **89** was not the product of the reaction.

Scheme 5.7 Expected Trapping of the Parent Phosphinidene Tungsten(0) Complex With Diphenylacetylene

Analysis of the product after purification revealed the product to be 1-cyclohexyl-2,3-diphenylphosphirene pentacarbonyltungsten(o) **90**.

Scheme 5.8 Generation of Terminal Phosphinidene Complex and Trapping With Diphenylacetylene

The molecular structure of the phosphirene tungsten(o) complex was also confirmed by single crystal X-ray diffraction analysis.

Figure 5.3 X-ray Crystal Structure of 1-Cyclohexylphosphirene Tungsten(0) Complex **90**. Main Distances (Å) and Angles (°): P1-W1 2.5061(12), P1-C6 1.851(4), P1-C18 1.792(4), P1-C19 1.793(4), C18-C19 1.325(6); C6-P1-C18 108.6(2), C6-P1-C19 109.7(2), C18-P1-C19 43.40(19)

The initial suspicion was that the parent phosphinidene was generated and trapped, and a subsequent hydrophosphination across the carbon-carbon double bond of cyclohexene took place. However, when conducted in the presence of twenty equivalents of diphenylacetylene, no trace of the vinylic phosphirene was observed.

It seemed that the secondary phosphirane was converted to the terminal cyclohexylphosphinidene complex **91** by migration of the hydrogen atom on to one of the bridging carbons in this bicyclic structure.

Scheme 5.9 Isomerization of Secondary Phosphirane Tungsten(0) Complex Into Cyclohexylphosphinidene Tungsten(0) Complex

To check the feasibility of such a transformation, a DFT calculation was performed on both **88** and **91** at the B3LYP/6-31G(d)-LanL2DZ(W) level.²⁰ It was found that the terminal phosphinidene complex **91** was only 11.1 kcal mol⁻¹ higher in energy than secondary phosphirane tungsten(o) complex **88**. The optimised structures of **91** and **88** are seen below.

Figure 5.4 Computed Structure of Cyclohexylphosphinidene Tungsten(0) Complex **91**

Figure 5.5 Computed Structure of Secondary Phosphirane Tungsten(0) Complex **88**

The reaction of **88** with *trans*-stilbene yielded the corresponding phosphirane tungsten(o) complex.

Scheme 5.10 Generation of Cyclohexylphosphinidene Tungsten(0) Complex and Subsequent Trapping with *trans*-Stilbene

The orientation of the olefin is maintained and the *trans*-disposition of the phenyl rings can be seen in the X-ray crystal structure.

Figure 5.6 X-ray Crystal Structure of 1-Cyclohexylphosphirane Tungsten(0) Complex **92**. Main Distances (Å) and Angles (°): P1-W1 2.476(2), P1-C6 1.836(7), P1-C18 1.860(7), P1-C19 1.832(7), C18-C19 1.532(10); C6-P1-C18 106.1(5), C6-P1-C19 105.2(5), C18-P1-C19 48.7(3)

Scheme 5.11 Generation of Cyclohexylphosphinidene Tungsten(0) Complex and Trapping With Styrene

We have also utilised styrene as a trapping agent, giving two diastereomeric phosphirane tungsten(o) complexes.

Single crystals of the minor product **93b** suitable for X-ray crystal structure analysis were grown from a saturated hexane solution at -25 °C and it revealed that, as expected, the major product had the phenyl moiety *syn* to the cyclohexyl ring and *anti* to the sterically imposing pentacarbonyltungsten(o) complexing group. The X-ray crystal structure can be found below.

Figure 5.7 X-ray Crystal Structure of 1-Cyclohexylphosphirane Tungsten(0) Complex **93b**. Main Distances (Å) and Angles (°): P1-W1 2.5079(17), P1-C6 1.824(7), P1-C7 1.858(7), P1-C14 1.856(6), C6-C7 1.529(10); C6-P1-C14 107.6(3), C7-P1-C14 108.3(3), C6-P1-C7 49.1(3)

We initially assumed that since the proton of the secondary phosphine tungsten(o) complex is slightly acidic, this reaction took place *via* an ionic mechanism. This hypothesis was checked by running a variable temperature NMR of phosphirane complex **88**. However, this possibility was quickly ruled out; at elevated temperatures, the phosphorus-hydrogen coupling constant remained constant at around 341 Hz and no coalescence was observed.

Figure 5.8 VT NMR of Secondary Phosphirane Complex **88**. Spectra Acquired at Room Temperature (Top) and 50 °C (Bottom)

To prove the generality of the reaction and to (possibly) shed some light into a plausible mechanism, a non-symmetrical phosphirane tungsten(o) complex was prepared. Heating a toluene solution of **87** with a large excess of 2-methylpropene, yielded phosphirane tungsten(o) complex **94**.

Scheme 5.12 Synthesis of 1-Chlorophosphirane Tungsten(0) Complex

Reduction of **94** with tributyltin hydride under the established reaction conditions yielded secondary phosphirane tungsten(o) complex **95**.

Scheme 5.13 Reduction of P-Cl Bond With $HSnBu_3$

95 was an interesting secondary phosphirane tungsten(o) complex. There were two pathways that could be undertaken; migration of the hydrogen to the secondary carbon, forming a terminal *tert*butylphosphinidene complex *via* TS1, or migration of the hydrogen to the quaternary carbon, forming the terminal *isobutyl*phosphinidene complex *via* TS2. When heated to 110 °C in the presence of diphenylacetylene, the reaction was extremely clean, forming the 1-*isobutyl*phosphirene complex exclusively.

Scheme 5.14 Selective Formation of 1-(*isobutyl*)phosphirane Tungsten(0) Complex

This selectivity for the concerted hydrogen-shift was investigated by DFT studies at the B3LYP/6-31G(d)-LanL2DZ(W) level.²⁰ When compared to the

can be seen in Figure 5.9.

Figure 5.9 Transition State For Isomerization of **95**

The conversion of secondary phosphirane complexes to terminal phosphinidene complexes is a new activation mode in the generation of these transient species. It is the only example of a terminal phosphinidene complex formation where no by-product is produced. This reaction is the equivalent of a reductive elimination of an alkane from an alkyl metal hydride.

The question arose: were we able to perform the opposite reaction, namely the conversion of terminal phosphinidene complexes to secondary phosphirane complexes? After all, the opposite reaction (oxidative addition) is present in transition metal chemistry,²¹ and it is known that some main group elements do behave as transition metals.²² Furthermore, both the forward and backward reaction must go by the same transition state, according to the principle of microscopic reversibility.²³

Scheme 5.15 Potential Synthesis of Phosphirane Complexes From Terminal Phosphinidene Complexes

To this end, we prepared 1-ethylphosphole pentacarbonyltungsten(o) **99** by quenching of tungsten(o) phospholide **15** with ethyl iodide.

Scheme 5.16 Synthesis of 1-Ethylphosphole Tungsten(0) Complex

99 was reacted with five equivalents of DMAD, giving the corresponding 7-ethyl-7-phosphanorbornadiene tungsten(o) complex **100**.

Scheme 5.17 Synthesis of 7-Ethyl-7-Phosphanorbornadiene Tungsten(0) Complex

Thermolysis of **100** at 110 °C caused decomposition, probably yielding ethylphosphinidene pentacarbonyltungsten(o) complex **97**. Unfortunately, no new signal at high field was observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, suggesting that insertion into the carbon-hydrogen bond did not take place.

Scheme 5.18 Thermolysis of 7-Ethyl-7-Phosphanorbornadiene Tungsten(0) Complex

To check if the presence of copper(I) chloride could induce the reaction, we repeated the reaction with the addition of copper(I) chloride as a catalyst at 55 °C but the results were identical.

Scheme 5.19 CuCl-Catalysed Decomposition of 7-Ethyl-7-Phosphanorbornadiene Tungsten(0) Complex

Trying to impart some stabilization, we thought of grafting a phenyl group on the terminal end of the phosphole substituent. Using (2-bromoethyl)benzene as an electrophile, 1-(β -phenylethyl)phosphole tungsten(o) complex **101** was synthesized from tungsten(o) phospholide **15** and subsequently treated with DMAD to form 7-(β -phenylethyl)-7-phosphanorbornadiene tungsten(o) complex **102**.

Scheme 5.20 Synthesis of 7-(β -Phenylethyl)-7-Phosphanorbornadiene Tungsten(0) Complex

Unfortunately when **102** was heated to 110 °C, only decomposition was observed.

Scheme 5.21 Thermal Decomposition of 7-(β -Phenylethyl)-7-Phosphanorbornadiene Tungsten(0) Complex

In order to induce an insertion, an electron withdrawing group was added on to the phenyl ring in an attempt to reduce the electron density on the carbon; 4-nitrophenethyl bromide was used as an electrophile. The results were

totally unexpected, seemingly forming 1-bromophosphole tungsten(o) complex **104**.

Scheme 5.22 Unexpected Generation of 1-Bromophosphole Tungsten(0) Complex

The exact structure of **104** cannot be verified with absolute certainty. The formulation was made on the basis of its chemical shift (1-chlorophosphole tungsten(o) complex **1** has a chemical shift of +72 ppm). We also know that it does not tolerate chromatography at -10 °C, forming a product with an electronegative group directly bonded to the phosphorus atom. The mechanism of formation of **104** is unclear and no hypothesis can be made at this current time.

5.3 Conclusion

In conclusion, we describe an unprecedented isomerization of secondary phosphiranes into terminal phosphinidene complexes. This takes place by a concerted hydrogen shift on to a neighbouring carbon atom. This is the only generation mode of terminal phosphinidene complexes with no by-product being formed and is analogous to a reductive elimination of alkanes from transition metal alkylhydrides.

5.4 Experimental Details

5.4.1 General Considerations

All reactions with air- or moisture-sensitive manipulations were carried out under positive pressure of nitrogen using standard Schlenk techniques. Tetrahydrofuran was distilled from sodium-benzophenone, toluene was distilled from sodium, dichloromethane was distilled from phosphorus pentoxide and hexane was distilled from sodium. All other solvents were used as received. Column chromatography was performed on Silica Gel (40-63 microns). NMR spectra were recorded on a Bruker Avance 500 spectrometer (500 MHz for ^1H , 125 MHz for ^{13}C , 202 MHz for ^{31}P), Bruker Avance 400 spectrometer (400 MHz for ^1H , 100 MHz for ^{13}C , 162 MHz for ^{31}P) or Bruker Avance III 400 spectrometer (400 MHz for ^1H , 100 MHz for ^{13}C , 162 MHz for ^{31}P). Chemical shifts are reported in δ (ppm), referenced to the residual solvent resonance of d_2 -dichloromethane for ^1H NMR ($\delta = 5.32$) and ^{13}C NMR ($\delta = 53.84$), CDCl_3 for ^1H NMR ($\delta = 7.26$) and ^{13}C NMR ($\delta = 77.00$) or d_6 -acetone for ^1H NMR ($\delta = 2.05$). ^{31}P chemical shifts are referenced to an external standard of 85% H_3PO_4 in H_2O ($\delta = 0.00$) and are uncorrected. Multiplicities are given as: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), m (multiplet). The number of protons (n) for a given resonance are given by $n\text{H}$ and coupling constants are given as a J value in Hz. Mass spectra were recorded on a JEOL AccuTOF-DART HRMS.

5.4.2 Experimental Procedures

1

1-Chloro-3,4-dimethylphosphole pentacarbonyltungsten(o) (**1**)

To a solution of hexachloroethane (7.8g, 33 mmol) was added a solution of **15** (from 5.5 mmol of **17** in THF (20 mL) in a dropwise manner. The solution was left stirring for 2 hours, concentrated and chromatographed over silica gel at -10 °C with hexane, yielding a bright orange solid.

$^{31}\text{P}\{^1\text{H}\}$ NMR (161 MHz, CDCl_3): δ 72.81 (s, $^1J_{\text{P-W}} = 245$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 16.7 (d, $^3J_{\text{P-C}} = 13.0$ Hz, 2C, - CH_3), 129.9 (d, $^1J_{\text{P-C}} = 37.0$ Hz, 2C, P-C), 150.5 (d, $^2J_{\text{P-C}} = 12.0$ Hz, 2C, -C- CH_3), 194.7 (d, $^2J_{\text{P-C}} = 7.0$ Hz, 4C, *cis*-CO), 198.1 (d, $^2J_{\text{P-C}} = 27.0$ Hz, 1C, *trans*-CO); ^1H NMR (400 MHz, CDCl_3): δ 2.18 (s, 6H, - CH_3), 6.38 (d, $^2J_{\text{P-H}} = 41.2$ Hz, 2H, PCH)

87

7-Chloro-7-phosphabicyclo[4.1.0]heptane pentacarbonyltungsten(o) (**87**)

To **1** (0.470 g, 1 mmol) was dissolved in toluene (5 mL). DMAD (0.50 mL, 4 mmol), cyclohexene (6.07 mL, 60 mmol) was added and heated to 75 °C. The mixture was cooled, concentrated and purified over silica at -10 °C with hexane to yield a pale yellow solid.

$^{31}\text{P}\{^1\text{H}\}$ NMR (161 MHz, CDCl_3): δ -65.35 (s, $^1J_{\text{P-W}} = 295$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 21.1 (d, $^2J_{\text{P-C}} = 3.6$ Hz, 2C, $-\text{CH}_3$), 21.7 (d, $^3J_{\text{P-C}} = 3.0$ Hz, 2C, P-C), 27.8 (d, $^1J_{\text{P-C}} = 21.9$ Hz, 2C, $-\text{CH}$), 194.7 (d, $^2J_{\text{P-C}} = 7.0$ Hz, 4C, *cis*-CO), 197.1 (d, $^2J_{\text{P-C}} = 42.0$ Hz, 1C, *trans*-CO)

$^{31}\text{P}\{^1\text{H}\}$ NMR (161 MHz, CDCl_3): δ -64.44 (s, $^1J_{\text{P-W}} = 295$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 19.4 (d, $^2J_{\text{P-C}} = 5.7$ Hz, 2C, $-\text{CH}_3$), 21.3 (d, $^3J_{\text{P-C}} = 1.8$ Hz, 2C, P-C), 23.1 (d, $^1J_{\text{P-C}} = 20.6$ Hz, 2C, $-\text{CH}$), 194.8 (d, $^2J_{\text{P-C}} = 8.0$ Hz, 4C, *cis*-CO), 198.1 (d, $^2J_{\text{P-C}} = 27.0$ Hz, 1C, *trans*-CO)

7-Phospha-bicyclo[4.1.0]heptane pentacarbonyltungsten(o) (**88a** & **88b**)

To a solution of **87** (47.2 mg, 0.1 mmol) in dry THF (1 mL) was added tributyltin hydride (53.8 μL , 0.2 mmol). The mixture was heated at 50 °C for 15h under an inert atmosphere. Upon completion of the reaction, the mixture was chromatographed directly over silica gel (-10 °C) with hexanes as the eluent, yielding a pale-grey solid. (25.8 mg, 59% yield).

88a: $^{31}\text{P}\{^1\text{H}\}$ NMR (161 MHz, CDCl_3): δ -215.28 (s, $^1J_{\text{P-W}} = 245$ Hz); ^{31}P NMR (161 MHz, CDCl_3): δ -215.3 (d, $^1J_{\text{P-H}} = 341$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 20.7 (d, $J_{\text{P-C}} = 6.9$ Hz, 2C, CH_2), 20.8 (d, $J_{\text{P-C}} = 3.1$ Hz, 2C, CH_2), 22.0 (d, $J_{\text{P-C}} = 2.6$ Hz, 2C, CH_2), 195.2 (d, $^2J_{\text{P-C}} = 7.9$ Hz, 4C, *cis*-CO), 197.6 (d, $^2J_{\text{P-C}} = 30.1$ Hz, 1C, *trans*-CO)

88b: $^{31}\text{P}\{^1\text{H}\}$ NMR (161 MHz, CDCl_3): δ -219.49 (s, $^1J_{\text{P-W}} = 250$ Hz); ^{31}P NMR (161 MHz, CDCl_3): δ -219.5 (d, $^1J_{\text{P-H}} = 341$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ

15.3 (d, $J_{P-C} = 12.6$ Hz, 2C, CH₂), 21.3 (d, $J_{P-C} = 3.2$ Hz, 2C, CH₂), 23.8 (d, $J_{P-C} = 5.7$ Hz, 2C, CH₂), 195.1 (d, $^2J_{P-C} = 7.7$ Hz, 4C, *cis*-CO), 197.0 (d, $^2J_{P-C} = 30.7$ Hz, 1C, *trans*-CO)

HRMS *m/z*: 437.9853 (calcd for C₁₁H₁₁O₅P¹⁸⁴W, 437.9854)

90

1-Cyclohexyl-2,3-diphenyl-1*H*-phosphirene pentacarbonyltungsten(o) (**90**)

To a solution of **88** (43.8 mg, 0.1 mmol) in dry toluene (1 mL) was added diphenylacetylene (71.3 mg, 0.4 mmol). The mixture was heated at 110 °C for 7h under an inert atmosphere. Upon completion of the reaction, the mixture was chromatographed directly over silica gel (-10 °C) with hexanes as the eluent, yielding a white solid (15.7 mg, 37% yield).

³¹P{¹H} NMR (161 MHz, CDCl₃): δ -141.37 (s, $^1J_{P-W} = 250$ Hz); ¹³C NMR (100 MHz, CDCl₃) δ 25.6 (s, 2C, CH₂), 26.5 (d, $J_{P-C} = 12.3$ Hz, 1C, PCH), 30.2 (s, 2C, CH₂), 46.1 (s, 1C, CH₂), 128.5 (d, $^2J_{P-C} = 6.8$ Hz, 1C, *ipso*-C), 128.8 (d, $^1J_{P-C} = 11.4$ Hz, 2C, P-C=C), 129.2 (s, 2C, *meta*-C), 130.2 (d, $J_{P-C} = 4.5$ Hz, 2C, *ortho*-C), 130.3 (s, 1C, *para*-C), 196.4 (d, $^2J_{P-C} = 7.9$ Hz, 4C, *cis*-CO), 198.2 (d, $^2J_{P-C} = 29.0$ Hz, 1C, *trans*-CO); ¹H NMR (400 MHz, CD₂Cl₂): δ 1.02-1.13 (m, 3H, Cy-*H*), 1.20-1.30 (m, 3H, Cy-*H*), 1.71-1.93 (m, 5H, Cy-*H*), 7.50-7.60 (m, 6H, Ar-*H*), 7.92 (d, $^3J_{P-H} = 7.2$ Hz, 4H, *ortho*-*H*)

HRMS *m/z*: 616.0638 (calcd for C₂₅H₂₁O₅P¹⁸⁴W, 616.0636)

1-Cyclohexyl-2-phenylphosphirane pentacarbonyltungsten(o) (**93a** & **93b**)

To a solution of **88** (43.8 mg, 0.1 mmol) in dry toluene (1 mL) was added styrene (43.8 μ L, 0.4 mmol). The mixture was heated at 110 °C for 7h under an inert atmosphere. Upon completion of the reaction, the mixture of diastereomers was chromatographed directly over silica gel (-10 °C) with hexanes as the eluent, first yielding the major isomer (**4a**) as a white solid (19.2 mg, 36% yield) followed by the minor isomer (**4b**) as a white solid (10.5 mg, 20% yield) for a combined yield of 56%.

93a: $^{31}\text{P}\{^1\text{H}\}$ NMR (161 MHz, CD_2Cl_2): δ -152.13 (s, $^1J_{\text{P-W}} = 245$ Hz); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 13.0 (d, $^1J_{\text{P-C}} = 11.0$ Hz, 1C, P-CH-Ph), 25.8 (d, $J_{\text{P-C}} = 1.3$ Hz, 1C, Cy-C), 26.2 (d, $J_{\text{P-C}} = 14.9$ Hz, 1C, Cy-C), 26.6 (d, $J_{\text{P-C}} = 13.7$ Hz, 1C, Cy-C), 29.4 (d, $J_{\text{P-C}} = 5.6$ Hz, 1C, Cy-C), 29.8 (d, $J_{\text{P-C}} = 4.6$ Hz, 1C, Cy-C), 29.9 (d, $J_{\text{P-C}} = 16.0$ Hz, 1C, Cy-C), 36.1 (d, $^1J_{\text{P-C}} = 13.8$ Hz, 1C, P-CH₂), 127.2 (d, $^5J_{\text{P-C}} = 1.3$ Hz, 1C, *para*-C), 128.87-128.90 (m, 2C, *ortho*-C & *meta*-C), 135.4 (d, $^2J_{\text{P-C}} = 5.4$ Hz, 1C, *ipso*-C), 196.5 (d, $^2J_{\text{P-C}} = 7.9$ Hz, 4C, *cis*-CO), 198.3 (d, $^2J_{\text{P-C}} = 28.7$ Hz, 1C, *trans*-CO); ^1H NMR (400 MHz, d_6 -Acetone): δ 0.70-0.75 (m, 1H), 0.96-1.21 (m, 5H), 1.42-1.54 (m, 3H), 1.73-1.79 (m, 3H), 2.33 (q, $J = 8.0$ Hz, 1H), 3.15 (t, $J = 9.2$ Hz, 1H), 7.26-7.48 (m, 5H)

93b: $^{31}\text{P}\{^1\text{H}\}$ NMR (161 MHz, CD_2Cl_2): δ -138.88 (s, $^1J_{\text{P-W}} = 254$ Hz); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 13.6 (d, $^1J_{\text{P-C}} = 13.0$ Hz, 1C, P-CH-Ph), 26.0 (s, 1C, Cy-C), 26.8-27.2 (m, 3C, Cy-C), 30.2 (s, 1C, Cy-C), 43.5 (d, $^1J_{\text{P-C}} = 12.0$ Hz,

1C, P-CH₂), 127.3 (s, 1C, *para*-C), 129.0 (s, 2C), 129.3 (s, 2C), 137.6 (s, 1C, *ipso*-C), 195.9 (d, ²J_{P-C} = 8.0 Hz, 4C, *cis*-CO), 197.8 (d, ²J_{P-C} = 29.0 Hz, 1C, *trans*-CO); ¹H NMR (400 MHz, d₆-Acetone): δ 1.31-1.47 (m, 7H), 1.70 (d, J = 12.4 Hz, 1H), 1.81-1.89 (m, 3H), 1.98 (d, J = 8.0 Hz, 1H), 2.07-2.16 (m, 2H), 3.21 (q, J = 10.0 Hz, 1H), 7.21-7.35 (m, 5H, Ar-H)

HRMS m/z: 542.0485 (calcd for C₁₉H₁₉O₅P¹⁸⁴W, 542.0480)

1-Chloro-2,2-dimethylphosphirane pentacarbonyltungsten(o) (**94**)

To **87** (0.410 g, 0.868 mmol) was added isobutene (15% in THF, 52 mmol). The solution was heated at 90 °C for 8h under an inert, closed atmosphere. Upon completion of the reaction, the mixture was chromatographed directly over silica gel (-10 °C) with hexanes as the eluent affording the product as a light yellow solid (0.305 g, 79 % yield)

³¹P{¹H} NMR (161 MHz, CDCl₃): δ -57.437(s, ¹J_{P-W} = 291 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 22.4 (d, ²J_{P-C} = 2.7 Hz, 1C, PC(CH₃)₂), 25.3 (d, ²J_{P-C} = 10.7 Hz, 1C, PC(CH₃)₂), 28.2 (d, ¹J_{P-C} = 21.0 Hz, 1C, PC(CH₃)₂), 28.8 (d, ¹J_{P-C} = 21.5 Hz, 1C, PCH₂), 194.7 (d, ²J_{P-C} = 8.2 Hz, 4C *cis*-CO), 197.5 (d, ²J_{P-C} = 42.2 Hz, 1C, *trans*-CO); ¹H NMR (400 MHz, CDCl₃): δ 1.29 (d, ³J_{P-H} = 23.3 Hz, 3H, PC(CH₃)₂), 1.31-1.34 (m, 1H, PCH₂), 1.68 (dd, ²J_{P-H} = 9.2 Hz, ²J_{H-H} = 5.6 Hz, 1H, PCH₂), 1.73 (d, ³J_{P-H} = 13.3 Hz, 3H, PC(CH₃)₂)

HRMS m/z: 445.9287 (calcd for C₉H₈O₅P³⁵Cl¹⁸⁴W, 445.9307)

2,2-Dimethylphosphirane pentacarbonyltungsten(0) (**95**)

To a solution of **94** (74.2 mg, 0.166 mmol) in dry THF (2 mL) was added tributyltin hydride (135 μ L, 0.5 mmol). The mixture was heated at 50 °C for 15h under an inert atmosphere. Upon completion of the reaction, the mixture was chromatographed directly over silica gel (-10 °C) with hexanes as the eluent, yielding a pale-yellow solid. (17.9 mg, 26% yield).

$^{31}\text{P}\{^1\text{H}\}$ NMR (161 MHz, CDCl_3): δ -198.65 (s, $^1\text{J}_{\text{P-W}} = 245$ Hz); ^{31}P NMR (161 MHz, CDCl_3): δ -198.6 (d, $^1\text{J}_{\text{P-H}} = 339$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 19.3 (d, $^1\text{J}_{\text{P-C}} = 12.1$ Hz, 1C, PCH_2), 23.2 (d, $^1\text{J}_{\text{P-C}} = 10.5$ Hz, 1C, $\text{PC}(\text{CH}_3)_2$), 24.3 (d, $^2\text{J}_{\text{P-C}} = 7.3$ Hz, 1C, $\text{PC}(\text{CH}_3)_2$), 28.1 (d, $^2\text{J}_{\text{P-C}} = 3.2$ Hz, 1C, $\text{PC}(\text{CH}_3)_2$), 195.1 (d, $^2\text{J}_{\text{P-C}} = 8.0$ Hz, 4C *cis*-CO), 197.3 (d, $^2\text{J}_{\text{P-C}} = 30.4$ Hz, 1C, *trans*-CO)

HRMS m/z : 411.9695 (calcd for $\text{C}_9\text{H}_9\text{O}_5\text{P}^{184}\text{W}$, 411.9697)

1-Isobutyl-2,3-diphenylphosphirene pentacarbonyltungsten(o) (**96**)

To a solution of **95** (17.9 mg, 0.043 mmol) in dry toluene (1 mL) was added diphenylacetylene (38.7 mg, 0.217 mmol). The mixture was heated at 110 °C for 7h under an inert atmosphere. Upon completion of the reaction, the mixture was chromatographed directly over silica gel (-10 °C) with hexanes as the eluent, yielding a white solid (8.8 mg, 34% yield).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3): δ -156.12 (s, $^1J_{\text{P-W}} = 256$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 23.7 (d, $^3J_{\text{P-C}} = 9.7$ Hz, 2C, $\text{PCH}_2\text{CH}(\text{CH}_3)_2$), 25.7 (s, 1C, $\text{PCH}_2\text{CH}(\text{CH}_3)_2$), 47.6 (s, 1C, $\text{PCH}_2\text{CH}(\text{CH}_3)_2$), 128.4 (d, 1C, $^2J_{\text{P-C}} = 6.7$ Hz, *ipso-C*), 129.3 (s, 2C, *meta-C*), 129.9 (d, $^3J_{\text{P-C}} = 4.9$ Hz, 2C, *ortho-C*), 130.3 (d, $^1J_{\text{P-C}} = 10.5$ Hz, 2C $\text{P-C}=\text{C}$), 130.4 (s, 1C, *para-C*), 196.3 (d, $^2J_{\text{P-C}} = 8.4$ Hz, 4C *cis-CO*), 198.1 (d, $^2J_{\text{P-C}} = 30.1$ Hz, 1C, *trans-CO*). ^1H NMR (400 MHz, CDCl_3): δ 0.94 (d, $^3J_{\text{H-H}} = 6.4$ Hz, 6H, $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 1.74-1.80 (m, 1H, $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 1.87 (d, $^3J_{\text{H-H}} = 6.3$ Hz, 2H, $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 7.49-7.58 (m, 6H, Ar-H), 7.87-7.89 (m, 4H, Ar-H)

HRMS m/z : 590.0471 (calcd for $\text{C}_{23}\text{H}_{19}\text{O}_5\text{P}^{184}\text{W}$, 590.0480)

991-Ethyl-3,4-dimethylphosphole pentacarbonyltungsten(o) (**99**)

Ethylbromide (0.88 mL, 11 mmol) was added to a solution of **15** (from 5.5 mmol of **17**) and stirred for 1.5 hours at room temperature. Upon completion, the mixture was concentrated and chromatographed over silica with hexane at -10 °C yielding a yellow solid.

$^{31}\text{P}\{^1\text{H}\}$ NMR (161 MHz, CDCl_3): δ 8.28 (s, $^1J_{\text{P-W}} = 208$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 9.8 (d, $^2J_{\text{P-C}} = 3.0$ Hz, 1C, $-\text{CH}_2\text{CH}_3$), 17.0 (d, $^3J_{\text{P-C}} = 11.0$ Hz, 2C, $-\text{CH}_3$), 23.3 (d, $^1J_{\text{P-C}} = 26.0$ Hz, 1C, $-\text{CH}_2\text{CH}_3$), 128.2 (d, $^1J_{\text{P-C}} = 41.0$ Hz, 2C, P-C), 151.1 (d, $^2J_{\text{P-C}} = 8.0$ Hz, 2C, $-\text{C}-\text{CH}_3$), 196.2 (d, $^2J_{\text{P-C}} = 7.0$ Hz, 4C, *cis*-CO), 199.3 (d, $^2J_{\text{P-C}} = 17.0$ Hz, 1C, *trans*-CO); ^1H NMR (400 MHz, CDCl_3): δ 1.00-1.08 (m, 3H, $-\text{CH}_2\text{CH}_3$), 1.97-2.04 (m, 2H, $-\text{CH}_2\text{CH}_3$), 2.18 (s, 6H, $-\text{CH}_3$), 6.29 (d, $^2J_{\text{P-H}} = 36.4$ Hz, 2H, PCH)

1007-Ethyl-7-phosphanorbornadiene pentacarbonyltungsten(o) (**100**)

To a solution of **99** (0.4641 g, 1 mmol) in toluene (2 mL) was added DMAD (0.50 mL, 4 mmol) and heated to 85 °C for 18 hours. Upon completion of the

reaction, the solution was cooled, concentrated and chromatographed over silica gel at -10 °C with hexane/EA to yield a pale yellow solid.

$^{31}\text{P}\{^1\text{H}\}$ NMR (161 MHz, CDCl_3): δ 220.0 (s, $^1J_{\text{P-W}} = 235$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 8.8 (s, 1C, $-\text{CH}_2\text{CH}_3$), 16.0 (s, 2C, $-\text{CH}_3$), 28.5 (s, 1C, $-\text{CH}_2\text{CH}_3$), 52.5 (s, 2C, $-\text{OCH}_3$), 58.5 (d, $^1J_{\text{P-C}} = 20.0$ Hz, 2C, PCH), 138.5 (d, $^2J_{\text{P-C}} = 16.0$ Hz, 2C, $\text{C}=\text{C}-\text{CH}_3$), 145.2 (d, $^2J_{\text{P-C}} = 5.0$ Hz, 2C, $-\text{C}=\text{CCO}$), 165.18 (d, $^3J_{\text{P-C}} = 3.0$ Hz, 2C, $\text{C}=\text{O}$), 196.1 (d, $^2J_{\text{P-C}} = 4.0$ Hz, 4C, *cis*-CO), 197.7 (d, $^2J_{\text{P-C}} = 26.0$ Hz, 1C, *trans*-CO); ^1H NMR (400 MHz, CDCl_3): δ 1.05-1.13 (m, 3H, $-\text{CH}_2\text{CH}_3$), 1.95 (s, 6H, $-\text{CH}_3$), 2.22-2.30 (m, 2H, $-\text{CH}_2\text{CH}_3$), 3.57 (d, $^2J_{\text{P-H}} = 2.8$ Hz, 2H, PCH), 3.82 (s, 6H, $-\text{COOCH}_3$)

101

1-(β-Phenylethyl)-3,4-dimethylphosphole pentacarbonyltungsten(o) (**101**)

(2-Bromoethyl)benzene (1.50 mL, 11 mmol) was added to a solution of **15** (from 5.5 mmol of **17**) and stirred for 1.5 hours at room temperature. Upon completion, the mixture was concentrated and chromatographed over silica with hexane at -10 °C yielding a yellow solid.

$^{31}\text{P}\{^1\text{H}\}$ NMR (161 MHz, CDCl_3): δ 4.23 (s, $^1J_{\text{P-W}} = 208$ Hz); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 17.5 (d, $^3J_{\text{P-C}} = 11.3$ Hz, 2C, $-\text{CH}_3$), 32.3 (d, $^2J_{\text{P-C}} = 3.8$ Hz, 1C, $-\text{PCH}_2$), 32.4 (s, 1C, $-\text{PCH}_2\text{CH}_2$), 126.9 (s, 1C, Ar-C), 128.6 (s, 2C, PCH), 128.7 (s, 2C, Ar-C), 129.1 (s, 2C, Ar-C), 141.9 (d, $^1J_{\text{P-C}} = 12.5$ Hz, 2C, Ar-C), 152.4 (d, $^2J_{\text{P-C}} = 7.5$ Hz, 2C, $-\text{C}-\text{CH}_3$), 196.1 (d, $^2J_{\text{P-C}} = 6.3$ Hz, 4C, *cis*-CO), 200.1 (d, $^2J_{\text{P-}}$

$c = 17.5$ Hz, 1C, *trans*-CO); ^1H NMR (400 MHz, CDCl_3): δ 2.17 (s, 6H, $-\text{CH}_3$), 2.28-2.29 (m, 2H, $-\text{PCH}_2\text{CH}_2$), 2.63-2.67 (m, 2H, $-\text{PCH}_2\text{CH}_2$), 6.31 (d, $^2J_{\text{P-H}} = 37.0$ Hz, 2H, PCH), 7.15-7.31 (m, 5H, Ar-*H*)

102

7-(β-Phenylethyl)-7-phosphanorbornadiene (**102**)

To a solution of **101** (0.4641 g, 1 mmol) in toluene (2 mL) was added DMAD (0.50 mL, 4 mmol) and heated to 85 °C for 18 hours. Upon completion of the reaction, the solution was cooled, concentrated and chromatographed over silica gel at -10 °C with hexane/EA to yield a pale yellow solid.

$^{31}\text{P}\{^1\text{H}\}$ NMR (161 MHz, CDCl_3): δ 213.1 (s, $^1J_{\text{P-W}} = 234$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 16.2 (d, $^3J_{\text{P-C}} = 1.3$ Hz, 2C, $-\text{CH}_3$), 32.4 (s, 1C, $-\text{CH}_2\text{CH}_3$), 38.3 (s, 1C, $-\text{CH}_2\text{CH}_3$), 52.8 (s, 2C, $-\text{OCH}_3$), 59.3 (d, $^1J_{\text{P-C}} = 18.7$ Hz, 2C, PCH), 126.9 (s, 1C, Ar-C), 128.6 (s, 2C, Ar-C), 129.2 (d, $^2J_{\text{P-C}} = 16.2$ Hz, 2C, Ar-C), 139.1 (d, $^2J_{\text{P-C}} = 16.2$ Hz, 2C, $\text{C}=\text{C}-\text{CH}_3$), 141.2 (d, $^3J_{\text{P-C}} = 12.5$ Hz, 1C, Ar-C), 145.7 (d, $^2J_{\text{P-C}} = 5.0$ Hz, 2C, $-\text{C}=\text{CCO}$), 165.5 (d, $^3J_{\text{P-C}} = 2.5$ Hz, 2C, $\text{C}=\text{O}$), 196.8 (d, $^2J_{\text{P-C}} = 7.5$ Hz, 4C, *cis*-CO), 198.4 (d, $^2J_{\text{P-C}} = 25.0$ Hz, 1C, *trans*-CO); ^1H NMR (400 MHz, CDCl_3): δ 2.00 (s, 6H, $-\text{CH}_3$), 2.54-2.57 (m, 3H, $-\text{PCH}_2\text{CH}_2$), 2.77-2.82 (m, 2H, $-\text{PCH}_2\text{CH}_2$), 3.56 (d, $^2J_{\text{P-H}} = 2.5$ Hz, 2H, PCH), 3.83 (s, 6H, $-\text{COOCH}_3$), 7.21-7.24 (m, 3H, Ar-*H*), 7.30-7.33 (m, 2H, Ar-*H*)

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Appendix

Crystallographic analyses were performed by Dr. Li Yongxin and Dr. Rakesh Ganguly at the Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University. The structures have been deposited into database of The Cambridge Crystallographic Data Centre (CCDC) and can be obtained free of charge.

Table A1 Crystal and Structural Refinement Data for **13**

CCDC number	1567743	
Identification code	mat231m	
Chemical formula	C ₁₂ H ₈ F ₃ O ₅ PW	
Formula weight	504.00 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.080 x 0.120 x 0.400 mm	
Crystal habit	yellow needle	
Crystal system	orthorhombic	
Space group	P n a 21	
Unit cell dimensions	a = 20.5816(4) Å	$\alpha = 90^\circ$
	b = 6.4805(2) Å	$\beta = 90^\circ$
	c = 22.8289(5) Å	$\gamma = 90^\circ$
Volume	3044.90(13) Å ³	
Z	8	
Density (calculated)	2.199 g/cm ³	
Absorption coefficient	7.743 mm ⁻¹	
F(000)	1888	
Theta range for data collection	2.17 to 36.35°	
Index ranges	-34 ≤ h ≤ 34, -10 ≤ k ≤ 10, -38 ≤ l ≤ 37	
Reflections collected	41787	
Independent reflections	13973 [R(int) = 0.0489]	
Coverage of independent reflections	99.4%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.5760 and 0.1480	
Structure solution technique	direct methods	
Structure solution program	XT, VERSION 2014/5	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\sum w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	13973 / 1 / 402	
Goodness-of-fit on F²	1.028	
$\Delta/\sigma_{\max}$	0.001	
Final R indices	11633 data; I > 2σ(I)	R1 = 0.0348, wR2 = 0.0470
	all data	R1 = 0.0521, wR2 = 0.0521
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0097P)^2 + 0.4147P]$ where $P = (F_o^2 + 2F_c^2)/3$	
Absolute structure parameter	0.433(8)	
Largest diff. peak and hole	1.350 and -1.326 eÅ ⁻³	
R.M.S. deviation from mean	0.225 eÅ ⁻³

Table A2 Crystal and Structural Refinement Data for **19**

CCDC number	1567744	
Identification code	mat233m	
Chemical formula	C ₂₀ H ₁₀ F ₃ O ₅ PW	
Formula weight	602.10 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.196 x 0.267 x 0.290 mm	
Crystal habit	colorless block	
Crystal system	orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 19.3956(4) Å	$\alpha = 90^\circ$
	b = 10.4487(2) Å	$\beta = 90^\circ$
	c = 20.1103(4) Å	$\gamma = 90^\circ$
Volume	4075.53(14) Å ³	
Z	8	
Density (calculated)	1.963 g/cm ³	
Absorption coefficient	5.803 mm ⁻¹	
F(000)	2288	
Theta range for data collection	2.87 to 33.16°	
Index ranges	-29 ≤ h ≤ 29, -16 ≤ k ≤ 16, -29 ≤ l ≤ 30	
Reflections collected	97085	
Independent reflections	7750 [R(int) = 0.0352]	
Coverage of independent reflections	99.7%	
Absorption correction	Numerical Mu Calculated	
Max. and min. transmission	0.3960 and 0.2840	
Structure solution technique	direct methods	
Structure solution program	XS, VERSION 2013/1	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\sum w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	7750 / 0 / 271	
Goodness-of-fit on F²	1.253	
$\Delta/\sigma_{\max}$	0.001	
Final R indices	6293 data; I > 2σ(I)	R1 = 0.0250, wR2 = 0.0452
	all data	R1 = 0.0365, wR2 = 0.0495
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + 9.1256P]$ where $P = (F_o^2 + 2F_c^2)/3$	
Largest diff. peak and hole	0.770 and -1.057 eÅ ⁻³	
R.M.S. deviation from mean	0.110 eÅ ⁻³

Table A3 Crystal and Structural Refinement Data for **22**

CCDC number	1567745
Identification code	mat234m
Chemical formula	C ₁₂ H ₁₀ F ₃ O ₅ PW
Formula weight	506.02 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.020 x 0.030 x 0.320 mm
Crystal habit	colorless needle
Crystal system	monoclinic
Space group	P 1 21/c 1
Unit cell dimensions	a = 6.5446(2) Å α = 90° b = 12.5563(4) Å β = 93.6681(12)° c = 17.9292(5) Å γ = 90°
Volume	1470.33(8) Å ³
Z	4
Density (calculated)	2.286 g/cm ³
Absorption coefficient	8.018 mm ⁻¹
F(000)	952
Theta range for data collection	2.28 to 35.14°
Index ranges	-10 ≤ h ≤ 10, -20 ≤ k ≤ 20, -28 ≤ l ≤ 28
Reflections collected	40767
Independent reflections	6369 [R(int) = 0.0806]
Coverage of independent reflections	97.3%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8560 and 0.1830
Structure solution technique	direct methods
Structure solution program	XT, VERSION 2014/5
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	6369 / 0 / 199
Goodness-of-fit on F²	1.019
$\Delta/\sigma_{\max}$	0.001
Final R indices	5048 data; R1 = 0.0377, wR2 = 0.0684 I > 2σ(I) all data R1 = 0.0550, wR2 = 0.0746
Weighting scheme	w = 1/[σ ² (F _o ²) + (0.0223P) ² + 3.5880P] where P = (F _o ² + 2F _c ²)/3
Largest diff. peak and hole	2.930 and -2.229 eÅ ⁻³
R.M.S. deviation from mean	0.243 eÅ ⁻³

Table A4 Crystal and Structural Refinement Data for **25**

CCDC number	1859858
Identification code	mat222
Chemical formula	C ₂₃ H ₁₇ O ₇ PW
Formula weight	620.18 g/mol
Temperature	203(2) K
Wavelength	0.71073 Å
Crystal size	0.080 x 0.140 x 0.180 mm
Crystal habit	yellow block
Crystal system	monoclinic
Space group	P 1 21/m 1
Unit cell dimensions	a = 9.8261(3) Å α = 90° b = 12.8512(3) Å β = 116.5041(9)° c = 9.9126(3) Å γ = 90°
Volume	1120.18(6) Å ³
Z	2
Density (calculated)	1.839 g/cm ³
Absorption coefficient	5.269 mm ⁻¹
F(000)	600
Theta range for data collection	2.30 to 31.18°
Index ranges	-14 ≤ h ≤ 14, -18 ≤ k ≤ 18, -14 ≤ l ≤ 14
Reflections collected	23522
Independent reflections	3768 [R(int) = 0.0309]
Coverage of independent reflections	99.8%
Absorption correction	Multi-Scan
Max. and min. transmission	0.6780 and 0.4510
Structure solution technique	direct methods
Structure solution program	XS, VERSION 2013/1
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	Σ w(F _o ² - F _c ²) ²
Data / restraints / parameters	3768 / 0 / 155
Goodness-of-fit on F²	1.104
Δ/σ_{max}	0.001
Final R indices	3498 data; R1 = 0.0172, wR2 = 0.0384 I > 2σ(I) all data R1 = 0.0205, wR2 = 0.0394
Weighting scheme	w = 1/[σ ² (F _o ²) + (0.0172P) ² + 0.3123P] where P = (F _o ² + 2F _c ²)/3
Largest diff. peak and hole	0.508 and -0.668 eÅ ⁻³
R.M.S. deviation from mean	0.093 eÅ ⁻³

Table A5 Crystal and Structural Refinement Data for **27**

CCDC number	1859897
Identification code	leung1030m
Chemical formula	C ₂₇ H ₂₇ O ₈ PW
Formula weight	694.30 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.040 x 0.100 x 0.240 mm
Crystal habit	colorless needle
Crystal system	triclinic
Space group	P -1
Unit cell dimensions	a = 7.1889(10) Å α = 104.219(4)° b = 13.2827(19) Å β = 96.454(4)° c = 15.393(2) Å γ = 98.162(4)°
Volume	1393.7(3) Å ³
Z	2
Density (calculated)	1.655 g/cm ³
Absorption coefficient	4.247 mm ⁻¹
F(000)	684
Theta range for data collection	2.76 to 25.12°
Index ranges	-8 ≤ h ≤ 8, -15 ≤ k ≤ 15, -18 ≤ l ≤ 18
Reflections collected	44781
Independent reflections	4969 [R(int) = 0.2226]
Coverage of independent reflections	99.8%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8480 and 0.4290
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)
Function minimized	Σ w(F _o ² - F _c ²) ²
Data / restraints / parameters	4969 / 0 / 339
Goodness-of-fit on F²	1.034
Final R indices	3382 data; R1 = 0.0605, wR2 = 0.1068 I > 2σ(I)
	all data R1 = 0.1106, wR2 = 0.1301
Weighting scheme	w = 1/[σ ² (F _o ²) + (0.0349P) ² + 5.2470P] where P = (F _o ² + 2F _c ²)/3
Largest diff. peak and hole	2.170 and -1.318 eÅ ⁻³
R.M.S. deviation from mean	0.193 eÅ ⁻³

Table A6 Crystal and Structural Refinement Data for **28**

CCDC number	1859898
Identification code	leung1000m
Chemical formula	C _{25.50} H ₂₂ Cl _{0.50} O ₇ PW
Formula weight	672.97 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.040 x 0.120 x 0.200 mm
Crystal habit	colorless plate
Crystal system	triclinic
Space group	P -1
Unit cell dimensions	a = 10.3051(8) Å α = 100.396(2)° b = 11.3322(8) Å β = 107.775(2)° c = 12.5787(9) Å γ = 92.243(3)°
Volume	1368.87(17) Å ³
Z	2
Density (calculated)	1.633 g/cm ³
Absorption coefficient	4.366 mm ⁻¹
F(000)	657
Theta range for data collection	2.25 to 29.63°
Index ranges	-13 ≤ h ≤ 14, -15 ≤ k ≤ 15, -17 ≤ l ≤ 17
Reflections collected	22263
Independent reflections	7684 [R(int) = 0.1252]
Coverage of independent reflections	99.5%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8450 and 0.4750
Structure solution technique	direct methods
Structure solution program	XT, VERSION 2014/5
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)
Function minimized	Σ w(F _o ² - F _c ²) ²
Data / restraints / parameters	7684 / 7 / 329
Goodness-of-fit on F²	1.018
Δ/σ_{max}	0.001
Final R indices	4412 data; I > 2σ(I) R1 = 0.0662, wR2 = 0.1124 all data R1 = 0.1455, wR2 = 0.1439
Weighting scheme	w = 1/[σ ² (F _o ²) + (0.0436P) ²] where P = (F _o ² + 2F _c ²)/3
Largest diff. peak and hole	1.273 and -1.568 eÅ ⁻³
R.M.S. deviation from mean	0.244 eÅ ⁻³

Table A7 Crystal and Structural Refinement Data for **30**

CCDC number	1859901
Identification code	leung1021m
Chemical formula	C ₁₄ H ₁₆ O ₂
Formula weight	216.27 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.140 x 0.180 x 0.260 mm
Crystal habit	colorless block
Crystal system	monoclinic
Space group	P 1 21/c 1
Unit cell dimensions	a = 15.8177(10) Å α = 90° b = 10.9590(7) Å β = 98.648(2)° c = 6.6787(4) Å γ = 90°
Volume	1144.56(12) Å ³
Z	4
Density (calculated)	1.255 g/cm ³
Absorption coefficient	0.082 mm ⁻¹
F(000)	464
Theta range for data collection	2.27 to 33.26°
Index ranges	-24 ≤ h ≤ 24, -16 ≤ k ≤ 16, -8 ≤ l ≤ 10
Reflections collected	33187
Independent reflections	4392 [R(int) = 0.0594]
Coverage of independent reflections	99.6%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9890 and 0.9790
Structure solution technique	direct methods
Structure solution program	XS, VERSION 2013/1
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)
Function minimized	Σ w(F _o ² - F _c ²) ²
Data / restraints / parameters	4392 / 0 / 149
Goodness-of-fit on F²	1.030
Final R indices	3125 data; I > 2σ(I) R1 = 0.0521, wR2 = 0.1354 all data R1 = 0.0800, wR2 = 0.1555
Weighting scheme	w = 1/[σ ² (F _o ²) + (0.0732P) ² + 0.3425P] where P = (F _o ² + 2F _c ²)/3
Largest diff. peak and hole	0.321 and -0.286 eÅ ⁻³
R.M.S. deviation from mean	0.064 eÅ ⁻³

Table A8 Crystal and Structural Refinement Data for **35**

CCDC number	1859902	
Identification code	leung1050m	
Chemical formula	C ₂₀ H ₁₉ O ₇ PW	
Formula weight	586.17 g/mol	
Temperature	105(2) K	
Wavelength	0.71073 Å	
Crystal size	0.040 x 0.060 x 0.240 mm	
Crystal habit	colorless needle	
Crystal system	monoclinic	
Space group	C 1 2/m 1	
Unit cell dimensions	a = 21.6451(6) Å	$\alpha = 90^\circ$
	b = 13.5218(4) Å	$\beta = 125.9548(13)^\circ$
	c = 18.2164(9) Å	$\gamma = 90^\circ$
Volume	4315.8(3) Å ³	
Z	8	
Density (calculated)	1.804 g/cm ³	
Absorption coefficient	5.464 mm ⁻¹	
F(000)	2272	
Theta range for data collection	2.72 to 31.00°	
Index ranges	-31 ≤ h ≤ 31, -14 ≤ k ≤ 19, -26 ≤ l ≤ 26	
Reflections collected	37671	
Independent reflections	7155 [R(int) = 0.1134]	
Coverage of independent reflections	99.9%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.8110 and 0.3540	
Structure solution technique	direct methods	
Structure solution program	XT, VERSION 2014/5	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	7155 / 0 / 287	
Goodness-of-fit on F²	1.037	
$\Delta/\sigma_{\max}$	0.001	
Final R indices	4587 data; I > 2σ(I)	R1 = 0.0514, wR2 = 0.0813
	all data	R1 = 0.1049, wR2 = 0.1007
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0240P)^2 + 26.1581P]$ where $P = (F_o^2 + 2F_c^2)/3$	
Largest diff. peak and hole	1.891 and -2.417 eÅ ⁻³	
R.M.S. deviation from mean	0.252 eÅ ⁻³

Table A9 Crystal and Structural Refinement Data for **37**

CCDC number	1859920	
Identification code	mat153s	
Chemical formula	C ₂₃ H ₁₉ O ₉ PW	
Formula weight	654.20 g/mol	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.140 x 0.180 x 0.260 mm	
Crystal system	monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 13.3165(4) Å	$\alpha = 90^\circ$
	b = 9.0103(3) Å	$\beta = 102.4210(10)^\circ$
	c = 20.8676(6) Å	$\gamma = 90^\circ$
Volume	2445.21(13) Å ³	
Z	4	
Density (calculated)	1.777 Mg/m ³	
Absorption coefficient	4.839 mm ⁻¹	
F(000)	1272	
Theta range for data collection	2.00 to 31.13°	
Index ranges	-19 ≤ h ≤ 18, -13 ≤ k ≤ 12, -29 ≤ l ≤ 13	
Reflections collected	32361	
Independent reflections	7829 [R(int) = 0.0291]	
Coverage of independent reflections	99.3%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.3897 and 0.2477	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7829 / 150 / 349	
Goodness-of-fit on F²	1.262	
Final R indices	I > 2σ(I)	R1 = 0.0216, wR2 = 0.0547
	all data	R1 = 0.0270, wR2 = 0.0712
Largest diff. peak and hole	1.040 and -1.405 eÅ ⁻³

Table A10 Crystal and Structural Refinement Data for **46**

CCDC number	1859921	
Identification code	leung1026m	
Chemical formula	C ₁₈ H ₁₇ O ₂ PS	
Formula weight	328.35 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.060 x 0.080 x 0.120 mm	
Crystal habit	colorless block	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 9.2601(5) Å	$\alpha = 90^\circ$
	b = 27.8195(16) Å	$\beta = 93.829(2)^\circ$
	c = 12.4529(6) Å	$\gamma = 90^\circ$
Volume	3200.8(3) Å ³	
Z	8	
Density (calculated)	1.363 g/cm ³	
Absorption coefficient	0.306 mm ⁻¹	
F(000)	1376	
Theta range for data collection	2.32 to 31.02°	
Index ranges	-13 ≤ h ≤ 12, -40 ≤ k ≤ 40, -17 ≤ l ≤ 18	
Reflections collected	50325	
Independent reflections	10197 [R(int) = 0.0924]	
Coverage of independent reflections	99.8%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9820 and 0.9640	
Structure solution technique	direct methods	
Structure solution program	XS, VERSION 2013/1	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	10197 / 0 / 401	
Goodness-of-fit on F²	1.031	
$\Delta/\sigma_{\max}$	0.001	
Final R indices	6842 data; I > 2σ(I)	R1 = 0.0527, wR2 = 0.1095
	all data	R1 = 0.0961, wR2 = 0.1317
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0466P)^2 + 1.6198P]$ where $P = (F_o^2 + 2F_c^2)/3$	
Largest diff. peak and hole	0.640 and -0.426 eÅ ⁻³	
R.M.S. deviation from mean	0.086 eÅ ⁻³

Table A11 Crystal and Structural Refinement Data for **47**

CCDC number	1859922	
Identification code	mat207	
Chemical formula	C ₁₆ H ₁₃ FeO ₄ P	
Formula weight	356.08 g/mol	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal size	0.120 x 0.160 x 0.180 mm	
Crystal habit	orange block	
Crystal system	monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 18.4900(11) Å	$\alpha = 90^\circ$
	b = 7.7134(4) Å	$\beta = 90.3140(18)^\circ$
	c = 22.4161(13) Å	$\gamma = 90^\circ$
Volume	3197.0(3) Å ³	
Z	8	
Density (calculated)	1.480 g/cm ³	
Absorption coefficient	1.057 mm ⁻¹	
F(000)	1456	
Theta range for data collection	1.82 to 30.60°	
Index ranges	-22 ≤ h ≤ 26, -11 ≤ k ≤ 11, -32 ≤ l ≤ 31	
Reflections collected	17929	
Independent reflections	4890 [R(int) = 0.0646]	
Coverage of independent reflections	99.5%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.8840 and 0.8330	
Structure solution technique	direct methods	
Structure solution program	XS, VERSION 2013/1	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	4890 / 0 / 201	
Goodness-of-fit on F²	1.026	
$\Delta/\sigma_{\max}$	0.001	
Final R indices	3749 data; I > 2σ(I)	R1 = 0.0404, wR2 = 0.0900
	all data	R1 = 0.0594, wR2 = 0.0992
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0368P)^2 + 0.7513P]$ where $P = (F_o^2 + 2F_c^2)/3$	
Largest diff. peak and hole	0.466 and -0.331 eÅ ⁻³	
R.M.S. deviation from mean	0.080 eÅ ⁻³

Table A12 Crystal and Structural Refinement Data for **59**

CCDC number	1832402	
Identification code	leung1020m	
Chemical formula	C ₂₇ H ₂₀ NO ₇ PW	
Formula weight	685.26 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.060 x 0.120 x 0.200 mm	
Crystal habit	colorless block	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.9398(2) Å	$\alpha = 104.7586(11)^\circ$
	b = 11.0344(3) Å	$\beta = 96.5743(10)^\circ$
	c = 15.8129(5) Å	$\gamma = 106.5191(10)^\circ$
Volume	1258.00(6) Å ³	
Z	2	
Density (calculated)	1.809 g/cm ³	
Absorption coefficient	4.703 mm ⁻¹	
F(000)	668	
Theta range for data collection	2.72 to 39.53°	
Index ranges	-14 ≤ h ≤ 14, -19 ≤ k ≤ 19, -28 ≤ l ≤ 28	
Reflections collected	80841	
Independent reflections	15051 [R(int) = 0.0675]	
Coverage of independent reflections	99.4%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.7660 and 0.4530	
Structure solution technique	direct methods	
Structure solution program	XT, VERSION 2014/5	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	15051 / 0 / 336	
Goodness-of-fit on F²	1.055	
$\Delta/\sigma_{\max}$	0.004	
Final R indices	12385 data; I > 2σ(I)	R1 = 0.0365, wR2 = 0.0556
	all data	R1 = 0.0551, wR2 = 0.0622
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0108P)^2 + 1.5605P]$ where $P = (F_o^2 + 2F_c^2)/3$	
Largest diff. peak and hole	2.042 and -2.134 eÅ ⁻³	
R.M.S. deviation from mean	0.218 eÅ ⁻³

Table A13 Crystal and Structural Refinement Data for **61**

CCDC number	1845376	
Identification code	leung1014m	
Chemical formula	C ₁₆ H ₁₃ NO ₂	
Formula weight	251.27 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.060 x 0.200 x 0.240 mm	
Crystal habit	colorless plate	
Crystal system	monoclinic	
Space group	P 1 2 ₁ /n 1	
Unit cell dimensions	a = 5.9036(2) Å	$\alpha = 90^\circ$
	b = 7.7981(3) Å	$\beta = 96.3197(18)^\circ$
	c = 26.5762(11) Å	$\gamma = 90^\circ$
Volume	1216.05(8) Å ³	
Z	4	
Density (calculated)	1.372 g/cm ³	
Absorption coefficient	0.091 mm ⁻¹	
F(000)	528	
Theta range for data collection	2.72 to 31.05°	
Index ranges	-8 ≤ h ≤ 7, -11 ≤ k ≤ 10, -38 ≤ l ≤ 38	
Reflections collected	11897	
Independent reflections	3852 [R(int) = 0.0708]	
Coverage of independent reflections	98.7%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9950 and 0.9780	
Structure solution technique	direct methods	
Structure solution program	XT, VERSION 2014/5	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3852 / 0 / 174	
Goodness-of-fit on F²	1.049	
$\Delta/\sigma_{\max}$	0.001	
Final R indices	2978 data; I > 2σ(I)	R1 = 0.0544, wR2 = 0.1343
	all data	R1 = 0.0738, wR2 = 0.1509
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0515P)^2 + 0.6745P]$ where $P = (F_o^2 + 2F_c^2)/3$	
Largest diff. peak and hole	0.487 and -0.325 eÅ ⁻³	
R.M.S. deviation from mean	0.065 eÅ ⁻³

Table A14 Crystal and Structural Refinement Data for **68**

CCDC number	183240	
Identification code	leung1037m	
Chemical formula	C ₂₂ H ₁₈ NO ₇ PW	
Formula weight	623.19 g/mol	
Temperature	140(2) K	
Wavelength	0.71073 Å	
Crystal size	0.020 x 0.140 x 0.180 mm	
Crystal habit	colorless plate	
Crystal system	monoclinic	
Space group	P 1 2 ₁ /c 1	
Unit cell dimensions	a = 9.8820(4) Å	$\alpha = 90^\circ$
	b = 9.4753(4) Å	$\beta = 91.7240(10)^\circ$
	c = 23.2307(9) Å	$\gamma = 90^\circ$
Volume	2174.22(15) Å ³	
Z	4	
Density (calculated)	1.904 g/cm ³	
Absorption coefficient	5.431 mm ⁻¹	
F(000)	1208	
Theta range for data collection	2.15 to 28.74°	
Index ranges	-13 ≤ h ≤ 13, -12 ≤ k ≤ 12, -31 ≤ l ≤ 31	
Reflections collected	38311	
Independent reflections	5711 [R(int) = 0.0665]	
Coverage of independent reflections	97.4%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.8990 and 0.4410	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)	
Function minimized	$\sum w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5711 / 0 / 293	
Goodness-of-fit on F²	1.295	
$\Delta/\sigma_{\max}$	0.001	
Final R indices	4872 data; I > 2σ(I)	R1 = 0.0389, wR2 = 0.0842
	all data	R1 = 0.0510, wR2 = 0.0917
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + 17.9969P]$ where $P = (F_o^2 + 2F_c^2)/3$	
Largest diff. peak and hole	2.769 and -1.887 eÅ ⁻³	
R.M.S. deviation from mean	0.295 eÅ ⁻³

Table A15 Crystal and Structural Refinement Data for **76**

CCDC number	1846727	
Identification code	leung1076m_0m_5	
Chemical formula	C ₁₃ H ₇ O ₆ PW	
Formula weight	474.01 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.020 x 0.120 x 0.200 mm	
Crystal habit	colorless plate	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 6.4473(3) Å	α = 80.3751(13)°
	b = 7.1659(3) Å	β = 89.0515(10)°
	c = 17.0031(7) Å	γ = 65.9150(10)°
Volume	705.90(5) Å ³	
Z	2	
Density (calculated)	2.230 g/cm ³	
Absorption coefficient	8.318 mm ⁻¹	
F(000)	444	
Theta range for data collection	3.16 to 37.77°	
Reflections collected	7349	
Coverage of independent reflections	98.1%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.8510 and 0.2870	
Structure solution technique	direct methods	
Structure solution program	XT, VERSION 2014/5	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)	
Function minimized	Σ w(F _o ² - F _c ²) ²	
Data / restraints / parameters	7349 / 3 / 197	
Goodness-of-fit on F²	1.030	
Final R indices	5658 data; I > 2σ(I)	R1 = 0.0482, wR2 = 0.0909
	all data	R1 = 0.0778, wR2 = 0.1054
Weighting scheme	w = 1/[σ ² (F _o ²) + (0.0347P) ² + 2.3183P] where P = (F _o ² + 2F _c ²)/3	
Largest diff. peak and hole	2.902 and -3.381 eÅ ⁻³	
R.M.S. deviation from mean	0.355 eÅ ⁻³

Table A16 Crystal and Structural Refinement Data for **88b**

CCDC number	1403839
Identification code	mat194
Chemical formula	C ₁₁ H ₁₁ O ₅ PW
Formula weight	438.02 g/mol
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal size	0.020 x 0.280 x 0.420 mm
Crystal habit	colorless plate
Crystal system	orthorhombic
Space group	P n m a
Unit cell dimensions	a = 19.4128(13) Å α = 90° b = 11.5970(8) Å β = 90° c = 5.9580 Å γ = 90°
Volume	1341.33(13) Å ³
Z	4
Density (calculated)	2.169 g/cm ³
Absorption coefficient	8.740 mm ⁻¹
F(000)	824
Theta range for data collection	3.58 to 36.48°
Index ranges	-24 ≤ h ≤ 32, -19 ≤ k ≤ 17, -9 ≤ l ≤ 9
Reflections collected	14805
Independent reflections	3388 [R(int) = 0.1247]
Coverage of independent reflections	99.4%
Absorption correction	multi-scan
Max. and min. transmission	0.8450 and 0.1200
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)
Function minimized	Σ w(F _o ² - F _c ²) ²
Data / restraints / parameters	3388 / 36 / 115
Goodness-of-fit on F²	1.025
Δ/σ_{max}	0.001
Final R indices	2614 data; R1 = 0.0553, wR2 = 0.1289 I > 2σ(I) all data R1 = 0.0739, wR2 = 0.1394
Weighting scheme	w = 1/[σ ² (F _o ²) + (0.0528P) ²] where P = (F _o ² + 2F _c ²)/3
Largest diff. peak and hole	3.509 and -4.572 eÅ ⁻³
R.M.S. deviation from mean	0.405 eÅ ⁻³

Table A17 Crystal and Structural Refinement Data for **90**

CCDC number	1403838
Identification code	mat192
Chemical formula	C ₂₅ H ₂₁ O ₅ PW
Formula weight	616.24 g/mol
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal size	0.060 x 0.120 x 0.420 mm
Crystal habit	colorless block
Crystal system	triclinic
Space group	P -1
Unit cell dimensions	a = 11.9182(5) Å α = 69.171(3)° b = 12.2880(5) Å β = 87.672(3)° c = 17.2709(7) Å γ = 87.278(3)°
Volume	2360.60(17) Å ³
Z	4
Density (calculated)	1.734 g/cm ³
Absorption coefficient	4.994 mm ⁻¹
F(000)	1200
Theta range for data collection	2.53 to 32.85°
Index ranges	-18 ≤ h ≤ 18, -18 ≤ k ≤ 18, -26 ≤ l ≤ 26
Reflections collected	85825
Independent reflections	17492 [R(int) = 0.1064]
Coverage of independent reflections	99.4%
Absorption correction	multi-scan
Max. and min. transmission	0.7540 and 0.2280
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)
Function minimized	Σ w(F _o ² - F _c ²) ²
Data / restraints / parameters	17492 / 0 / 577
Goodness-of-fit on F²	0.979
Δ/σ_{max}	0.002
Final R indices	11621 data; R1 = 0.0445, wR2 = 0.0770 I > 2σ(I) all data R1 = 0.0872, wR2 = 0.0905
Weighting scheme	w = 1/[σ ² (F _o ²) + (0.0267P) ²] where P = (F _o ² + 2F _c ²)/3
Largest diff. peak and hole	1.265 and -2.248 eÅ ⁻³
R.M.S. deviation from mean	0.226 eÅ ⁻³

Table A18 Crystal and Structural Refinement Data for **92**

CCDC number	1859948	
Identification code	mat193	
Chemical formula	$\text{C}_{24.66}\text{H}_{22.40}\text{Br}_{0.09}\text{O}_5\text{PW}$	
Formula weight	620.36 g/mol	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.100 x 0.220 x 0.240 mm	
Crystal habit	colorless block	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.1745(9) Å	$\alpha = 78.4732(12)^\circ$
	b = 12.0617(9) Å	$\beta = 81.2704(13)^\circ$
	c = 18.0216(14) Å	$\gamma = 89.9664(13)^\circ$
Volume	2351.3(3) Å ³	
Z	4	
Density (calculated)	1.752 g/cm ³	
Absorption coefficient	5.158 mm ⁻¹	
F(000)	1209	
Theta range for data collection	1.72 to 31.05°	
Reflections collected	14941	
Independent reflections	14941 [R(int) = 0.0491]	
Coverage of independent reflections	99.5%	
Absorption correction	multi-scan	
Max. and min. transmission	0.6270 and 0.3710	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)	
Function minimized	$\Sigma w(\text{Fo}^2 - \text{Fc}^2)^2$	
Data / restraints / parameters	14941 / 385 / 634	
Goodness-of-fit on F²	0.974	
$\Delta/\sigma_{\text{max}}$	0.002	
Final R indices	10997 data; I > 2σ(I)	R1 = 0.0471, wR2 = 0.1016
	all data	R1 = 0.0687, wR2 = 0.1097
Weighting scheme	$w = 1/[\sigma^2(\text{Fo}^2) + (0.0476\text{P})^2]$ where $\text{P} = (\text{Fo}^2 + 2\text{Fc}^2)/3$	
Largest diff. peak and hole	2.754 and -2.023 eÅ ⁻³	
R.M.S. deviation from mean	0.249 eÅ ⁻³

Table A19 Crystal and Structural Refinement Data for **93b**

CCDC number	1403840
Identification code	mat199
Chemical formula	C ₁₉ H ₁₉ O ₅ PW
Formula weight	542.16 g/mol
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal size	0.020 x 0.260 x 0.420 mm
Crystal habit	colorless plate
Crystal system	monoclinic
Space group	P 1 21/c 1
Unit cell dimensions	a = 9.668(3) Å α = 90° b = 30.873(9) Å β = 95.918(3)° c = 6.5271(19) Å γ = 90°
Volume	1937.8(10) Å ³
Z	4
Density (calculated)	1.858 g/cm ³
Absorption coefficient	6.069 mm ⁻¹
F(000)	1048
Theta range for data collection	6.56 to 30.84°
Index ranges	-13 ≤ h ≤ 13, -44 ≤ k ≤ 44, -6 ≤ l ≤ 9
Reflections collected	21659
Independent reflections	6019 [R(int) = 0.0663]
Coverage of independent reflections	98.7%
Absorption correction	multi-scan
Max. and min. transmission	0.8880 and 0.1850
Structure solution technique	direct methods
Structure solution program	SHELXT (Bruker AXS Inc., 2014)
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	Σ w(F _o ² - F _c ²) ²
Data / restraints / parameters	6019 / 0 / 235
Goodness-of-fit on F²	1.138
Δ/σ_{max}	0.002
Final R indices	4882 data; I > 2σ(I) R1 = 0.0556, wR2 = 0.1028 all data R1 = 0.0740, wR2 = 0.1081
Weighting scheme	w = 1/[σ ² (F _o ²) + (0.0001P) ² + 18.3600P] where P = (F _o ² + 2F _c ²)/3
Largest diff. peak and hole	2.088 and -5.139 eÅ ⁻³
R.M.S. deviation from mean	0.216 eÅ ⁻³