Advancing the chemistry of monovalent phosphorus

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2012

Duffy, M. P. (2012). Advancing the chemistry of monovalent phosphorus. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/50949>

<https://doi.org/10.32657/10356/50949>

ADVANCING THE CHEMISTRY OF MONOVALENT PHOSPHORUS

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

2012

ACKNOWLEDGEMENTS

I would like to first start off by expressing my deepest gratitude to all the mentors, teachers, and professors that have come into my life, that have taught, inspired, encouraged, and believed in me, for it is they who have helped paved the way for who I am today. I would like to thank my high school chemistry teacher, Mr. Kryder. For it was during his class that I realized, that whatever I was going to do in my life it was going to involve chemistry. I would like to thank my undergraduate professor, Dr. Roger Tatum, a brilliant, tough, and inspiring chemistry teacher, whose classes, such as general chemistry, inorganic, and instrumental analysis, were a joy to attend. I have learned so much from him. Other undergraduate teachers I would like to thank are Dr. Raymond Sheldon, Dr. Clyde Webster, and Dr. Marvin Payne. I would like to deeply thank Dr. Krista Motschiedler, a wonderful, kind-hearted teacher who allowed me to do organic chemistry research in her laboratory and was the first to give me a taste of research. Finally, I would like to express my deepest gratitude and respect to my PhD supervisor Professor François Mathey, for his patience, guidance, and encouragement throughout my PhD career. I am extremely appreciative for everything he has done for me, and my wife. He is a wonderful supervisor and teacher and I have learned much from him, not only inside the lab, but outside the lab as well. I truly cherish his friendship. As Henry Adams once said "A teacher affects eternity; he can never tell where his influence stops." And to all those wonderful teachers I would like to say, thank you.

I would also like to thank my colleagues for their help, discussions, and advice. From the University of California, Riverside, I would like to thank, Dr. Samia Estassi, Dr. Paul Richardson, Dr. Shohreh Rahbarnia, Dr. Magali Clochard, Dr. Irina Kalinina, Dr. Ngoc Hoa Tran Huy, Ana Ciric, and a special thanks to Dr. Aholibama Escobar. From

Nanyang Technological University, I would like to thank Dr. Luo Wei, Ng Kim Hong, Ng Yong Xiang, Feny Ho, Lin Yuhua, and a very special thanks to Dr. Tian “the crystal master” Rongqiang and Mao “the Emperor” Yanli.

I would like to acknowledge the help provided by all the undergraduate students that I have worked with, with a special thanks to Lin Yuhua, Feny Ho, Marion Janker, Leo Nicholls, Soh Mei Samantha, and Liow Yu Ting.

I would like to thank the staff at Nanyang Technological University, with a special thanks to Dr. Li Yongxin and Dr. Rakesh Ganguly for their assistance in X-ray crystallography; Ee Ling, for her help with NMR; and Celine, for all her assistance in graduate school matters.

I would like to thank Nanyang Technological University for financial support and for the funding to present my research at the 7th Workshop on Organic Chemistry for Junior Chemists in Hsinchu, Taiwan, and at the 8th International Conference on Inorganic Chemistry in Heidelberg, Germany.

Last, but not least, I would like to thank my wife, Evelyn, for her love, encouragement, and support. I could not have done it without her.

Matthew P. Duffy

August 2012

ABSTRACT

Advancing the Chemistry of Monovalent Phosphorus

Matthew P. Duffy

This thesis documents our attempts to advance the chemistry of monovalent phosphorus. To advance the chemistry of monovalent phosphorus one must incorporate new substituents on phosphorus, and/or find new substrates with which to trap the terminal phosphinidene complexes with. This thesis consists of seven chapters. Chapter one is an introduction to phosphinidene chemistry. It describes the transition from phosphinidene chemistry to terminal phosphinidene chemistry. Chapter one goes on to describe the different methods to generate terminal phosphinidene complexes, extensively lists reactions done with them, provides a brief overview of the types of reactions that they can do, and ends by describing ways of removing the transition metal from phosphorus of the newly generated organophosphorus species. Chapter two describes the generation and trapping of a chlorophosphinidene complex, which was achieved starting from an improved synthesis of 1-chloro-3,4-dimethylphosphole tungsten complex. Chapter three is a direct application of the chlorophosphinidene complex, which provides a straightforward synthesis to 2-phosphafurans, one of the least well-known members of the heterophosphole family. Also some preliminary results concerning its chemistry are provided. Chapter four describes the generation of a hydroxyphosphinidene complex and our attempts to use it as a source for making new phosphinous acids. With our new synthetic routes to the chlorophosphole and hydroxyphosphole, chapter five describes how we use these building blocks to generate P-X-P-linked biphosphole complexes (X = O, S). We discovered that a minor change in the structure leads to a complete shift from the [4+2] to the [2+2] dimerization. Chapter six describes the reaction of terminal phosphinidene complexes with dihydrogen, where the end product is similar to the reaction of dihydrogen and carbenes, although the reaction conditions are harsher and the mechanism of the reaction is quite different. Chapter seven describes the reaction of terminal phosphinidene complexes with silanes, which lead to primary phosphine complexes.

LIST OF PUBLICATIONS

1. *"Functionalization of Phospholide Ions: Expanding the Scope by Changing the Base."* Clochard, Magali; **Duffy, Matthew P.**; Donnadiou, Bruno; Mathey, François. *Organometallics*, **2008**, 27 (4), pp 567–570. Publication Date (Web): January 25, 2008
2. *"The Unexpected Chemistry of a Bis(phospholyl)acetylene."* **Duffy, Matthew P.**; Donnadiou, Bruno; Mathey, François. *Heteroatom Chemistry*, **2008**, 19 (5), pp 537-541. Publication Date: July 2008
3. *"Generation and Trapping of a Terminal Chlorophosphinidene Complex."* **Duffy, Matthew P.**; Mathey, François. *J. Am. Chem. Soc.*, **2009**, 131 (22), pp 7534–7535. Publication Date (Web): May 12, 2009
4. *"Synthesis and Chemistry of 2-Phosphafurans."* **Duffy, Matthew P.**; Lin, Yuhang.; Ho, Feny.; Mathey, François. *Organometallics*. **2010**, 29, 5757-5758. Publication Date (Web): October 14, 2010
5. *"Intramolecular [4+2] versus [2+2] cycloadditions in P-X-P-linked biphospholes (X=O,S)."* **Duffy, Matthew P.**; Lin, Yuhang; Liow, Yu Ting.; Mathey, François. *New J. Chem.*, **2011**, 35, 2001-2003. Publication Date (Web): April 18, 2011
6. *"The Reaction of Terminal Phosphinidene Complexes with Dihydrogen"* **Duffy, Matthew P.**; Liow, Yu Ting; Nicholls, Leo; Li, Yongxin; Ganguly, Rakesh; Mathey, François. *Organometallics*, **2012**, 31 (7), 2936-2939. Publication Date (Web): November 30, 2011

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ABBREVIATIONS AND SYMBOLS

δ	NMR chemical shift in Hz
$^{\circ}$	degrees
^{13}C	$^{13}\text{C}\{^1\text{H}\}$
^{31}P NMR	$^{31}\text{P}\{^1\text{H}\}$
7PNBD	7- phosphanorbornadiene
$\text{\AA}$	Angstroms
a.k.a	also known as
ASE	Aromatic Stabilization Energy
ca.	<i>circa</i> = approximately
calcd	calculated
cod	1,5-cyclooctadiene
Cp	cyclopentadiene
Cp*	1,2,3,4,5-Pentamethylcyclopentadiene
Cy	cyclohexane
d	doublet
DCM	dichloromethane
dd	doublet of doublets
Deg	degrees
DFT	Density functional theory
Dipp	2,6- <i>i</i> -Pr ₂ C ₆ H ₃
D.I.	deionized
DMAD	<u>dimethyl acetylenedicarboxylate</u>
DMF	dimethylformamide
DMSO	dimethyl sulfoxide

dppe	1,2-bis(diphenylphosphino)ethane
dt	doublet of triplets
e.g.	<i>exempli gratia</i> = example
et. al.	<i>et aliae</i> = and others
h	hours
Hex	hexane
HOMO	highest occupied molecular orbital
HRMS	High Resolution Mass Spectrometry
i.e	<i>id est</i> = that is
IUPAC	International Union of Pure and Applied Chemistry
kcal	kilocalorie
kJ	kilojoule
LUMO	lowest unoccupied molecular orbital
<i>m</i>	<i>meta</i>
m	multiplet
mol	mole
<i>m/z</i>	mass-to-charge ratio
NICS	nucleus-independent chemical shift
NMR	nuclear magnetic resonance
<i>o</i>	<i>ortho</i>
<i>p</i>	<i>para</i>
ppm	parts per milion
q	quartet
R_F	retardation factor or retention factor
RT	room temperature
SPOs	Secondary Phosphine Oxides

t	triplet
TBAF	tetra-n-butylammonium fluoride
THF	tetrahydrofuran
TOF	time of flight
Tol	toluene
TosOH	<i>p</i> -toluenesulfonic acid
Tp	tris(pyrazolyl)borate
ZPE	zero point energy

CHAPTER 1

Introduction to Phosphinidene Chemistry

Phosphinidenes^{1,2,3,4,5} (IUPAC recommended name: phosphanylidene) are unstable six-electron singly substituted species (R-P) that are analogous to carbenes⁶ ($R_2C:$). Early attempts to generate phosphinidenes were made by thermolysis of cyclopolyphosphanes, by reduction of dihalophosphanes, or by cycloreversion of phosphorus heterocycles. Attempts to trap phosphinidenes with cyclohexene, butadiene, and tolane (a.k.a. diphenylacetylene) had proven unsuccessful.^{7,8} In 1965, Schmidt et. al. confirmed their existence by successfully inserting phenylphosphinidene into a disulfide bond (Scheme 1.1).^{9,10}

Scheme 1.1 Schmidt's first successful trapping reactions of phenylphosphinidene with a disulfide bond.

Phosphinidenes exist in either the singlet or triplet state (Fig. 1.1), where the substituent R determines their preferred ground state and is reflected by the singlet-triplet energy gap (ΔE_{ST}).

Figure 1.1 Singlet and triplet phosphinidenes

According to high-level calculations, alkyl- and aryl- phosphinidenes favor the triplet ground state ($\Delta E_{ST} = -22$ to -26 kcal·mol⁻¹)^{11,12}. When there is a π -donating substituent, such as amino or phosphano groups, the π -substituent stabilizes the singlet state ($\text{Me}_2\text{N-P:}$ $\Delta E_{ST} = 1.7$ kcal·mol⁻¹, $(\text{CH}_3)_2\text{P-P:}$ $\Delta E_{ST} = 3.7$ kcal·mol⁻¹).¹³

Phosphinidenes differ from carbenes in the sense that instead of two substituents ($\text{R}_2\text{C:}$) they have only one (R-P:), plus an additional lone pair. This lone pair (or in the case of triplet phosphinidenes, the two unpaired electrons) can interact with a transition metal group (η^1 complex) for increased stability, while maintaining a carbene-like behavior. These η^1 -phosphinidenes, also known as terminal phosphinidenes, also relate to η^1 -carbene transition metal complexes. Electrophilic (*Fischer* type) phosphinidene complexes result from a singlet-singlet combination while the nucleophilic (*Schrock* type) phosphinidenes result from a triplet-triplet combination (Fig. 1.2).

Figure 1.2. Electrophilic and Nucleophilic Phosphinidenes

Both electrophilic and nucleophilic terminal phosphinidenes have been represented as $RP=ML_n$ in the literature. But this might not be the best representation. Since the electrophilic phosphinidenes results from two singlets, the electrophilic phosphinidene ligand is equivalent to a neutral two-electron donor (such as CO), thus the best representation for this complex would be $(RP \rightarrow ML_n)$ as suggested by Cowley and Barron.¹⁴ In this case, the oxidation state of phosphorus would be 1, and the system is polarized $P^{\delta+}M^{\delta-}$. Thus the electrophilic phosphinidene complexes are formally derived from monovalent phosphorus.

The nucleophilic phosphinidenes result from the combination of two triplets, resulting in a genuine $P=M$ double bond, $(RP=ML_n)$. In this case, the oxidation state of phosphorus is 3. In the $P=M$ double bond, the system is polarized $P^{\delta-}M^{\delta+}$ as a result of the higher electronegativity of phosphorus.

DFT calculations suggest that the philicity of the terminal phosphinidene is not so much influenced by the metal itself, but by the metal's spectator ligands (L).¹⁵ Strong π -acceptor ligands (e.g., CO) reduce the electron density on phosphorus, stabilize the π^* -orbital energy¹⁶, and enhance its electrophilicity. While, strong σ -donors (e.g., Cp) increase the electron density on phosphorus, raise the π^* -orbital energy, and thus enhance its nucleophilicity.

It should be mentioned that phosphinidenes give rise to seven different types of complexes all of which have been described in the literature (Fig. 1.3). In practice, only the η^1 bent terminal phosphinidenes have significant potential as synthetic tools in organophosphorus chemistry, and so will be discussed more in depth, with an emphasis on the electrophilic type.

Figure 1.3. The 7 Different Types of Phosphinidene Complexes

1.1 Electrophilic Terminal Phosphinidenes

Electrophilic phosphinidene complexes are derived from low oxidation state metallic centers that typically contain π -acceptor ligands (e.g., CO). As mentioned before the strong π -accepting CO ligands withdraw electron density and reduce the charge concentration on the phosphorus atom and thus enhance the electrophilicity of the phosphinidene complex. Theoretical studies of electrophilic phosphinidene complexes corroborate their preferred singlet nature and demonstrate that the singlet-triplet energy gap (ΔE_{ST}) increases with π -donation from the substituent on phosphorus [e.g. $\text{H-P} \rightarrow \text{W}(\text{CO})_5$: $\Delta E_{ST} = 9.3$, $\text{Ph-P} \rightarrow \text{W}(\text{CO})_5$: $\Delta E_{ST} = 10.3$, $\text{H}_2\text{N-P} \rightarrow \text{W}(\text{CO})_5$: $\Delta E_{ST} = 29.9$ kcal·mol⁻¹].¹⁷ The singlet reactivity of terminal phosphinidene complexes is further enhanced by metal-phosphorus π -back-donation into the empty p_{π^*} acceptor orbital on phosphorus (Fig. 1.2).

Since their discovery¹⁸ by Mathey in 1982, several methods have been used to synthesize these transient terminal phosphinidene complexes. Thermally induced cheletropic elimination¹⁹ of terminal electrophilic phosphinidene complexes from a variety of precursors has been inferred from numerous trapping experiments. Even though these transient species have eluded spectroscopic detection, their intermediacy is supported by kinetic studies that show the release of the phosphinidene complex to be a first-order process in the concentration of the 7-phosphanorbornadiene complexes²⁰ and the 3*H*-benzophosphepin complexes²¹, and with no dependence on the nature of the trapping reagent. Also, the [1+2] cycloaddition of terminal electrophilic phosphinidenes to *E*- and *Z*-substituted alkenes proceeds with complete retention of stereochemistry, suggesting a concerted reaction similar to that of singlet carbenes.²² The five known methods for generating electrophilic phosphinidene complexes will be described below.

1.1.1 Generation of electrophilic terminal phosphinidenes from 7-phosphanorbornadiene complexes

The original method¹⁸ used to access the neutral electrophilic terminal phosphinidenes **4** is still the most widely used (Scheme 1.2). It arises from the thermal decomposition of 7-phoshabicyclo[2.2.1]hepta-2,5-diene complexes (a.k.a. 7-phosphanorbornadiene complexes **2**, or 7-PNBD) to expel the terminal phosphinidene with the phthalate **3** formed as a side product. These 7-phosphanorbornadiene complexes can easily be made by a [4+2] cycloaddition of the substituted 1*H*-phosphole complex **1** with dimethyl acetylenedicarboxylate (DMAD).²³

Scheme 1.2 General reaction scheme for generating terminal phosphinidenes from 7-phosphanorbornadienes

While this scheme is, in practice, limited to M= Cr, Mo, W(CO)₅, and Fe(CO)₄, it is extremely versatile concerning the substituent R at the phosphorus atom. The only observed limitations are for: bulky R groups such as ^tBu, where the bulky substituent prevents the cycloaddition of the 1-*H*-phosphole diene and the C≡C bond of DMAD; or for amino groups, where the P-N bond adds across the electrophilic C≡C bond of DMAD.

This method of generating terminal phosphinidenes has been widely successful and has been applied for the incorporation of approximately 37 different substituents (including 2 new substituents resulting from the work of this thesis). An extensive list of terminal

phosphinidines generated from their 7-phosphanorbornadiene precursors and their reactions is given in Table 1.1.

Table 1.1 Terminal phosphinidenes [M-P-R] generated from metal complexed (M=W, Mo, Cr(CO)₅, or Fe(CO)₄) 7-phosphanorbornadiene precursors. [L] indicates if a CO ligand on the metal has been replaced. ^{Cu} indicates reactions using CuCl as a catalyst. [†] indicates if *N*-methyl imidazole has been used as a catalyst. Entries highlighted in **bold** are contributions based on this work.

Substituent	Reaction	Reference
WPPh	alkynes (diphenylacetylene, diethylacetylene), butadienes, methanol	18
	water, PhNH ₂ , Et ₂ NH	24
	methanol ^{Cu} , phenylacetylene ^{Cu} , alkenes (1-hexene, cyclohexene, cyclooctene, styrene, <i>trans</i> -stilbene, <i>cis</i> -stilbene) ^{Cu} , vinyl ether ^{Cu} (electron-rich olefin), butadienes ^{Cu} , cyclopentadiene ^{Cu} , α,β -unsaturated ketones ^{Cu}	22
	enamines	25
	alkynes (via 1-pot rxn from phosphole and DMAD), phenyl propiolates (PhCCCO ₂ Et = electron poor alkyne), 1,4-cyclohexadiene ^{Cu}	26
	no trapping reagent ^{Cu} = dimerization, alkenes, alkynes, PhNH ₂	20
	ferrocene ^{Cu}	27
	carbene ^{Cu} : (Ph)(EtO)C=W(CO) ₅	28
	three-membered heterocycles X=O,S,N	29
	carbenes ^{Cu} : (Ph)(EtO)C=Cr(CO) ₅ , (Ph) ₂ C=W(CO) ₅ , (OMe)(CH ₂ C(Me)C=W(CO) ₅ , (EtO)(PhCH=CH)C=Cr(CO) ₅	30
	<i>p</i> -X-substituted styrenes ^{Cu} (X= OCH ₃ , CH ₃ , Ph, H, F, Cl, Br)	31
	carbyne ^{Cu} : (Cp)(CO) ₂ W $\equiv$ C-Ph	32
	electron-rich alkynes: ethoxyacetylene, propynyldiethylamine ^{Cu}	33
	PBu ₃	34
	1-methoxy-1,3-cyclohexadiene ^{Cu}	35
	cyclohexadiene ^{Cu}	36
	norbornadienes ^{Cu} , norbornenes ^{Cu}	37
	exocyclic olefins ^{Cu}	38
	phosphaalkenes: RP=C(SiMe ₃) ₂	39
	alkyl substituted olefins ^{Cu}	40
	vinyl bromide, allyl bromide	41
	enolizable ketones, β -diketones	42

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cycloalkadienes ^{Cu}	43
allenes ^{Cu}	44
benzophenone ^{Cu} , fluorenone	45
no trapping reagent ^{Cu} = dimerization, no trapping reagent = trimerization, (PhP=PPh)(W(CO) ₅) ₃	46
substituted butadiynes ^{Cu} RCCCCR (R=CH ₂ OPh, Ph)	47
[5]metacyclophane ^{Cu}	48
<i>N</i> -methyl(benzylidene)amine ^{Cu} (Me-N=CH-Ph)	49
azobenzene	50
1,4-disubstituted-1,3-diynes (R= SiMe ₃ , ^t Bu)	51
conjugated diynes ^{Cu}	52
bicyclopropylidene ^{Cu}	53
2,5-dimethyl-2,4-hexadiene ^{Cu}	54
silene	55
dienes ^{Cu} , cisoid dienes ^{Cu}	56
cumulenes ^{Cu}	57
1-piperidinonitrile/DMAD	58
vinyl chlorides	59
phospholene ^{Cu} , phospholene, phosphole ^{Cu}	60
2,4,6-tri- <i>tert</i> -butyl-1,3,5-triphosphabenzene	61
imine (Ph-C=N-Ph), diimines	62
[W(CO) ₅]-complexed phosphole	63
bicycloalkylidenes ^{Cu}	64
bis(imine)	65
phosphorus ylides	66
(acetylmethylene)triphenylphosphorane: (Ph ₃ P=CHC(O)Me)	67
triphenylphosphonium cyanomethylide	68
triphenylphosphane-imino carbonitrile/DMAD	69
2nd-generation bicyclopropylidene ^{Cu} , 2nd-generation bicyclopropylidene	70
azulenes ^{Cu}	71
malonate anion	72
<i>N</i> -cyano- <i>P,P,P</i> -triphenylphosphazene (Ph ₃ P=N-CN)	73
cyclopropenes ^{Cu} , cyclopropenes	74
<i>N</i> -substituted-diphenylketenimines ^{Cu} (Ph ₂ C=C=N-R, R=Ph, ⁱ Pr, ^t Bu), bisketenimines	75
spirocyclopropanated methylenecyclopropanes ^{Cu} , bicyclopropylidenes ^{Cu}	76
CsF/18-Crown-6	77
thienyl-substituted alkynes ^{Cu} , thienyl-substituted alkynes	78

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	hexamethyl Dewar benzene ^{Cu} , hexamethyl Dewar benzene	79
	phosphaallene	80
	diallene ^{Cu} , diallene	81
	cyclopropenylidene	82
	bulky ynamine (PhC≡C-N ⁱ Pr ₂)	83
	Ph-C≡C-SiMe ₃ , Ph-C≡C-SnBu ₃	84
	H₂	85, This work
	silanes (PhSiH₃)	This work
WPMe	alkynes	18
	PhNH ₂	24
	ferrocene ^{Cu}	27
	Cp ₂ Ni ₂ (C ₂ R ₂) clusters ^{Cu} , Cp ₂ Ni ₂ (C ₂ R ₂) clusters	86
	PBu ₃	34
	<i>p</i> -X-substituted styrenes ^{Cu} (X= OCH ₃ , CH ₃ , Ph, H, Cl, Br)	87
	Rh=Rh: [Rh ₂ (η ⁵ -C ₅ Me ₅) ₂ (μ-(CO) ₂)] ^{Cu}	88
	exocyclic olefins ^{Cu}	38
	vinyl bromide, allyl bromide	41
	2-alkynyl-phosphirenes ^{Cu}	47
	Os=Os : [Os ₃ (μ ² -H)(CO) ₁₀] ^{Cu}	89
	<i>N</i> -methyl(benzylidene)amine ^{Cu} (Me-N=CH-Ph)	49
	azobenzene	50
	1-piperidinonitrile/DMAD	58
	phosphorus ylides	66
	allenes ^{Cu} (Me ₂ C=C=CH ₂), alkylidenephosphiranes	90
	(acetylmethylene)triphenylphosphorane (Ph ₃ P=CHC(O)Me)	67
	triphenylphosphane-imino carbonitrile/DMAD	69
	1,6-methano-[10]annulene ^{Cu}	91
	malonate anion	72
	<i>N</i> -substituted-diphenylketenimines ^{Cu} (Ph ₂ C=C=N-Ph)	75
	cyclooctatetraenes ^{Cu}	92
	bulky ynamine (PhC≡C-N ⁱ Pr ₂)	83
	no trapping reagent ^{Cu} = dimerization	93
	H₂	85, This work
WPCH ₂ Ph	2-alkynyl-phosphirenes ^{Cu}	47
WPCH ₂ Cl	methanol ^{Cu} , butadienes ^{Cu} , no trapping reagent ^{Cu} = rearrangement	94
	alkynes (diphenylacetylene)	95
WPCH ₂ CH ₂ Cl	alkynes ^{Cu} , alkynes	96
	ferrocene ^{Cu}	27

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	phosphaalkenes: $\text{RP}=\text{C}(\text{SiMe}_3)_2$	39
	malonate anion	72
	CsF/18-Crown-6	77
	$\text{PhC}\equiv\text{C}-\text{N}^i\text{Pr}_2^{\text{Cu}}$	97
$\text{WP}(\text{CH}_2)_n\text{Cl}$ $n=2-5$	PBU_3	98
$\text{WPCH}_2\text{CH}_2\text{CO}_2\text{Et}$	alkynes (diphenylacetylene)	99
	dimethyl cyanamide ^{Cu} , triphenylphosphane-imino carbonitrile/DMAD	69
	<i>N</i> -cyano-P,P,P-triphenylphosphazene ($\text{Ph}_3\text{P}=\text{N}-\text{CN}$)	73
	no trapping reagent ^{Cu} = dimerization	93
$\text{WP}(\text{CH}_2)_3\text{C}(\text{O})\text{Ph}$, $\text{WP}(\text{CH}_2)_n\text{C}(\text{O})\text{Me}$ $n=1,3,4$	PBU_3	100
WPCO_2Et	methanol ^{Cu} , Et_2NH , alkynes	101
	PBU_3 , PEt_3	34
$\text{WPCH}_2\text{CH}_2\text{CN}$	1-piperidino carbonitrile/DMAD, triphenylphosphane-imino carbonitrile/DMAD	69
WPCN	alkynes	101
$\text{WPCH}_2\text{CH}=\text{CH}_2$	alkynes ^{Cu} , alkenes ^{Cu}	102
	PBU_3	34
	2-alkynyl-phosphirenes ^{Cu}	47
$\text{WP}(\text{CH}_2)_2\text{CH}=\text{CH}_2$	alkynes ^{Cu}	102
$\text{WP}(\text{CH}_2)_3\text{CH}=\text{CH}_2$	Self-condensation ^{Cu}	102
$\text{WPCH}_2\text{CH}=\text{CHCH}_2\text{Cl}$	no trapping reagent ^{Cu} = rearrangement	103
$\text{WPC}(\text{Me})=\text{CH}_2$	no trapping reagent ^{Cu} = dimerization followed by cyclization	104
$\text{WPCH}=\text{CH}-\text{CH}=\text{CH}_2$	alkynes ^{Cu} , butadienes ^{Cu} , self-condensation ^{Cu}	105
WPCCPh	alkynes	106
$\text{WP}-(2\text{-}N\text{-methylpyrrolyl})$	no trapping reagent ^{Cu} = dimerization	93
$\text{WP}-(2\text{-thienyl})$	no trapping reagent ^{Cu} = dimerization	93
$\text{WP-9H-fluoren-9-yl}$	alkynes, methanol	101
WP-myrtanyl	alkynes, alkenes	107
$\text{WP}-(2'\text{-formyl-2-biphenyl})$	PBU_3	108
$\text{WPCH}_2\text{CH}_2\text{-[P(C}_2\text{Ph}_2\text{)W(CO)}_5\text{]}$	no trapping reagent = self-condensation	109

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WPOMe	methanol, Et ₂ NH, alkenes (<i>trans</i> -stilbene), alkynes (diphenylacetylene), 1-azadienes	110
	<i>p</i> -X-substitued styrenes ^{Cu} (X= OCH ₃ , CH ₃ , Ph, H, CF ₃ , Cl, Br)	111
	bulky ynamine (PhC≡C-N [†] Pr ₂)	83
	silanes (PhSiH₃, Me₂PhSiH)	This work
WPO ^t Bu	alkynes ^{Cu}	101
WPOH	alkynes	This work
WPCI	alkynes, alkenes, butadienes	112
	benzylideneacetophenone	113
	trimethylsilylacetylene	This work
WPCH ₂ CH ₂ PW	methanol	114
WP-Ph-Ph-PW	alkynes ^{Cu} , alkynes, methanol ^{Cu}	115
WPCH ₂ CH=CHCH ₂ PW (Z)	alkynes ^{Cu} , dienes ^{Cu}	116
W[PCH ₂ CH ₂ P]	methanol, Et ₂ NH, alkynes, alkenes	114
W[P(CH ₂) ₃ P]	alkynes	114
MoPPh	alkynes	117
	<i>N</i> -methyl(benzylidene)amine ^{Cu} (Me-N=CH-Ph)	118
	acetylenic alcohol (PhC≡CCH ₂ -OH)	119
	water [†] , ethanol [†] , ethylene glycol [†] , CCl ₄ [†] , no trapping reagent [†]	120
MoPMe	ferrocene ^{Cu}	27
MoPF	alkynes, butadienes	121
[L]MoPPh	L= 7-Ph-7PNBD ^{Cu} , 1-Ph-phospholene = intramolecular condensation, 1-Ph-phosphole = intramolecular condensation	63
[L]MoPPh	L= 7-membered phosphorus heterocycle cycloalkene containing C=C = intramolecular condensation	122
[L]MoPPh	(L= PMe ₃) alkynes, alkenes	123
CrPPh	alkynes	18
	methanol, water, PhNH ₂	24
	carbene ^{Cu} : Ph(OEt)C=W(CO) ₅	30
	no trapping reagent = trimers + tetramers	93
FePPh	diphenylacetylene (via 1-pot rxn of phosphole/DMAD)	26
	alkynes (diphenylacetylene, phenylacetylene), EtOH; (via 1-pot rxn of phosphole/DMAD)	124

If the 7-phosphanorbornadiene complex **2** is too reactive or displays too low a stability (such as when R=CN¹⁰¹, R= C≡C-Ph¹⁰⁶, R= Cl¹¹², or M= Fe(CO)₄²⁶) it is advantageous to use directly the mixture of phosphole complex/dimethyl

acetylenedicarboxylate (DMAD), as the phosphinidene precursor. Typically when the $M=W(CO)_5$, the decomposition (or breaking of the phosphorus bridge) takes place around 100-110°C. The decomposition temperature can be affected by the substituent on phosphorus, as well as the substrate (i.e. trapping agent).

Copper(I) chloride facilitates the fragmentation of the 7-phosphanorbornadienes tungsten complexes and can significantly lower the reaction temperature to 55-60°C.²² It does not catalyze the reaction when the complexed metal is chromium or molybdenum, a point that is not too often stressed and not well understood. It must be noted that in some instances it is possible for CuCl to alter the course of the reaction; such as causing rearrangements^{94,95} of the terminal phosphinidene, or effecting reactions with^{125,11,74,60} or without^{46,93} a substrate, i.e. the trapping reagent.

DFT calculations by Lammertsma et. al. suggest that the extrusion of phosphorus from the 7-phosphanorbornadiene complexes proceeds via a transition state where the copper is tricoordinated to W, P, and one of the bridgehead carbons.¹¹ Following the initial fragmentation, the $W(CO)_5PR-CuCl$ complex is then predicted to migrate a chloride from copper to phosphorus, with stabilization of the copper ion by a coordinating solvent (e.g. toluene). Then the trapping reagent (e.g. alkene) reacts with the phosphorus displacing the chloride back to copper in an S_N2 -like reaction (Scheme 1.3).¹¹

Scheme 1.3 Reaction of a 7-phosphanorbornadiene using CuCl as a catalyst depicting the DFT predicted phosphinidenoid complex **5** intermediate.

Thus based on Lammertsma's calculations, the reactive intermediate is a phosphinidenoid complex $[\text{W}(\text{CO})_5(\text{RP}(\text{Cu-L})\text{Cl})]$ **5** (where L = alkene or the solvent toluene). This phosphinidenoid complex, in analogy to carbenoids¹²⁶ (Fig. 1.4), would give the same product to that of a reaction with a terminal phosphinidene complex, but would be more sensitive to steric congestion and could alter the course of the reaction. Which could explain the occasional alternate reactions seen when CuCl is used as a catalyst, as mentioned earlier.

Figure 1.4. Terminal Phosphinidene Complex (I), Phosphinidenoid metal complex (II), Carbene (III), and Carbenoid (IV). R = organic substituent; M = metal, typically main group; X = halogen or leaving group; ML_n = transition metal complex

This as well as the isolated dimer **8**, from the reaction of 7-phosphanorbornadiene **6** with 2,5-dihydro-1*H*-phosphole **7** (Scheme 1.4) appear to support this phosphinidenoid complex.⁶⁰

Scheme 1.4 Reaction of 7-phosphanorbornadiene **6** with 2,5-dihydro-1*H*-phosphole **7** with CuCl to form the intermediate dimer **8**.

Streubel et. al. have obtained strong experimental evidence for a transient phosphinidenoid tungsten complex $[(\text{TMS}_2\text{HC})\text{P}(\text{X})\text{Li}(\text{12-crown-4})]\text{W}(\text{CO})_5$ ($\text{X} = \text{Cl}^{127}$, F^{128}). Its reaction with and without trapping reagents can be seen in Scheme 1.5.

Scheme 1.5 Reaction of phosphinidenoid tungsten complex **9** with and without trapping reagents.

Hammett reaction constants, ρ , have been determined for the CuCl -catalyzed addition to styrenes to give small, negative values [$\text{W}(\text{CO})_5\text{PPh}$: $\rho = -0.76$ (σ^+)³¹, $\text{W}(\text{CO})_5\text{PMe}$: $\rho = -0.60$ (σ^+)⁸⁷, $\text{W}(\text{CO})_5\text{POMe}$: $\rho = -0.60$ (σ^+)¹¹¹] which support the electrophilic carbene-like nature of the reactive intermediate. These values closely match the Hammett reaction constants of some free carbenes [$(\text{CH}_3)_2\text{C}=\text{C}$: $\rho = -0.75$ (σ)¹²⁹; Cl_2C : $\rho = -0.62$ (σ^+)¹³⁰, F_2C : $\rho = -0.57$ (σ^+)¹³¹].

Occasionally the substrate can facilitate the copper-catalyzed fragmentation of 7-phosphanorbornadienes to occur even at room temperature,⁷⁶ where the reaction rate can become dependent on the substrate concentration.⁵⁶ Deactivation of the catalyst can also occur, if the substrate forms stable, inactive copper(I) chloride complexes, as is typically observed for reagents containing phosphorus.⁶¹ For such substrates, generation of the terminal phosphinidene by noncatalyzed methods is

preferred. It should also be mentioned that it is possible for the substituent on phosphorus to deactivate the copper catalyst as well (e.g. $\text{CH}_2\text{CH}_2\text{CN}$)⁹³.

1.1.2 Generation of electrophilic terminal phosphinidenes from phosphirane complexes

The second method to generate terminal electrophilic phosphinidenes is from phosphiranes. The substituted metal complexed phosphirane undergoes chelotropic elimination (or in other words a [1+2] retroaddition) to give the terminal phosphinidene and ethylene (Scheme 1.6).

Scheme 1.6 Generating terminal phosphinidenes from phosphirane complexes

An extensive list of terminal phosphinidines generated from their substituted phosphiranes and their reactions is given in Table 1.2.

Table 1.2 Terminal phosphinidenes [M-P-R] generated from metal complexed (M=W(CO)₅, or Fe(CO)₄) substituted phosphiranes. Entries highlighted in **bold** are contributions based on this work.

Substituent	Reaction	Reference
WPPh	alkynes	20
WPCH=CHPh	alkynes	132
WPNEt ₂	alkynes, butadiene, alkenes	133
WPN(C ₆ H ₁₁) ₂	phosphaalkyne (P≡CCMe ₃)	134
WPNHPh	alkynes	135
	PhC≡C-N ^t Pr ₂	97
	H₂	85, This work
WPNH(o-	Phosphaalkynes (P≡C-R, R= ^t Bu, 1-Ad)	136

toly)		
WPCI	alkynes (diphenylacetylene)	133
	alkynes (diphenylacetylene, trimethylsilylacetylene), alkenes (styrene), ferrocene	This work
FePN ⁱ Pr ₂	N-substituted-diphenylketenimines (Ph ₂ C=C=N-Ph)	75

In 1985, Mathey et. al. showed that it was possible to generate a terminal phosphinidene from a complexed phosphirane.²⁰ They generated a phenylphosphinidene tungsten complex from 1,2,3-triphenylphosphirane tungsten pentacarbonyl, at 150°C and trapped it with diphenylacetylene. This kind of experiment was related to the work of Quast, who in 1982 demonstrated that *tert*-butylphosphinidene oxide could be generated thermally from tris-*tert*-butylphosphirane oxide.¹³⁷ At such high decomposition temperatures (150°C) this route for generating terminal phosphinidene complexes was far less useful than the 7-phosphanorbornadiene method. That is until in 1989, when Mathey et. al. showed that when changing the substituent of a complexed phosphirane from a hydrocarbon to an amino substituent, the temperature of generating the terminal phosphinidene dropped to 70-90°C.¹³³ The nitrogen lone pair more efficiently stabilizes the singlet state of the terminal phosphinidene. This method now provided a new route to amino substituted phosphinidenes complexes unlike the 7-phosphanorbornadiene method for reasons already mentioned. A few methods for generating metal complexed phosphiranes can be seen in schemes 1.7, 1.8, and 1.9.

Scheme 1.7 Generating a complexed phosphirane from the aminophosphine complex^{138,133}

Scheme 1.8 Generating a complexed phosphirane from the β -chloroethylphosphinidene complex^{139, 135}

Scheme 1.9 Generating a complexed phosphirane from the reaction of a terminal phosphinidene with an alkene⁷⁵

1.1.3 Generation of electrophilic terminal phosphinidenes from 3H-benzophosphepine complexes

The third method for generating terminal electrophilic phosphinidene complexes **4** is from 3H-benzophosphepine complexes **10** (Scheme 1.10).

Scheme 1.10 Generating a terminal phosphinidene from 3H-benzophosphepine

In 2005, Lammertsma et. al. discovered that upon heating, around $70-85^\circ C$, the 3H-benzophosphepine complex **10** undergoes a facile electrocyclic reaction to the unstable phosphanorcaradiene **11** and subsequently dissociates into the terminal phosphinidene complex **4** and naphthalene **12**.^{140, 21} An extensive list of terminal phosphinidines generated from their substituted 3H-benzophosphepine and their reactions is given in Table 1.3.

Table 1.3 Terminal phosphinidenes [ML_n-P-R] generated from metal complexed (ML_n=W(CO)₅, Mo(CO)₅, Cr(CO)₅, or Mn(Cp)(CO)₂) 3*H*-benzophosphepines.

Substituent	Reaction	Reference
WPPh	alkynes, styrene, butadiene, MeOH	140
	diphenyl-1,3-butadiyne, no trapping reagent	21
	hexamethyl Dewar benzene	79
	phosphaallene	80
	diallene	81
WPMe	alkynes, alkenes, aniline	21
	hexamethyl Dewar benzene	79
	phosphaallene	80
WP ^t Bu	alkynes	21
WP(<i>p</i> -C ₆ H ₅ -NMe ₃ OTf)	MeOH, alkyne, propene, 1,4-dioxene, ethylene	141
WPNET ₂	alkynes	21
MoPPh	alkynes	140
	<i>o</i> -diethynylbenzene	21
CrPPh	alkynes, alkenes	21
Mn(CO) ₂ (Cp)PPh	alkynes	140
	phenylacetylene, 1-hexene	21

3*H*-benzophosphepine complexes **10** are synthesized by a double hydrophosphination of 1,2-bis(ethynyl)benzene **13** with a metal complexed primary phosphine **14** (Scheme 1.11).¹⁴⁰

Scheme 1.11 Synthesis of 3*H*-benzophosphepine complexes

Since the phosphorus group is introduced in the final step of the formation of the phosphepine **10**, this method is more tolerant of other transition metal complexes (e.g. Mn(Cp)(CO)₂) as well as bulky groups (e.g. ^tBu) and amino substituents. Its limitation

lies in the feasibility of the synthesis of the metal complexed substituted primary phosphine **14**, which can prove difficult at times.

1.1.4 Generation of electrophilic terminal phosphinidenes from phosphirene complexes

The fourth method for generating terminal electrophilic phosphinidene complexes is from phosphirene metal complexes. Terminal phosphinidenes have been successfully generated from two types of phosphirenes: *1H*-phosphirene and *2H*-azaphosphirene complexes. In 1989, Mathey et. al. demonstrated that diethylaminophosphinidene tungsten complex **16** could be generated from [1-(diethylamino)-2,3-diphenylphosphirene] pentacarbonyltungsten **15** (Scheme 1.12).¹³³

Scheme 1.12 Generating a terminal phosphinidene from a *1H*-phosphirene

A list of terminal phosphinidenes generated from *1H*-phosphirenes and their reactions is given in Table 1.4.

Table 1.4 Generation of diethylaminophosphinidene complex from *1H*-phosphirenes.

Substituent	Reaction	Reference
WPNet ₂	butadiene, EtOH, HNet ₂	133

This method can produce terminal aminophosphinidenes from complexed aminophosphirenes but at significantly higher temperatures (130-140°C), than compared to complexed aminophosphiranes (70-90°C); this is also indicative of the

higher stability of phosphirenes over phosphiranes. Thus this method wasn't very practical until in 1994, when Streubel et. al. synthesized the first 2*H*-azaphosphirene tungsten complex **17**,¹⁴² and in 1995, demonstrated that a terminal phosphinidene complex **4** could be generated from it at around 45-75°C (Scheme 1.13).¹⁴³

Scheme 1.13 Generating a terminal phosphinidene from a 2*H*-azaphosphirene

Initially it was assumed that the terminal phosphinidene **4** was generated via the cleavage of both the P-C and P-N bonds in a concerted process. But later in 1997, Streubel et. al. recognized that it was actually a two-step process that starts with the cleavage of the P-C bond, giving the intermediate nitrilium-phosphine ylide **18**, which they were able to trap.¹⁴⁴

In 1999, they were also able to show that they could photochemically generate the nitrilium-phosphine ylide **18** at -50°C,¹⁴⁵ and at slightly warmer temperatures (-30°C) subsequently generate the terminal phosphinidene complex **4**.¹⁴⁶ An extensive list of terminal phosphinidenes generated from 2*H*-azaphosphirenes and their reactions is given in Table 1.5.

Table 1.5 Generation of terminal phosphinidenes from 2*H*-azaphosphirene complexes

Substituent	Reaction	Reference
WPCH(SiMe ₃) ₂	phenylacetylene, diphenylacetylene, benzaldehyde	143
	phosphaalkynes	147
	ethoxyacetylene, dimethyl acetylenedicarboxylate	148
	benzophenone, acetophenone, (<i>E</i>)- <i>N</i> -methyl(benzylidene)-amine	149
	acetylene derivatives	150
	alkynes, alkynes/substituted nitriles	151
	2- <i>H</i> -azaphosphirene	152

	CCl ₄ , water	153
	benzyl bromide, 2-bromopyridine, bromobenzene	154
	silylene	155
	isonitriles	146
	iodomethane, diiodomethane	156
	isocyanates	157
WPCp [*]	[Et ₃ NH]Cl	158
	alkynes	159
	aldehydes	160
MoPCH(SiMe ₃) ₂	alkynes, alkynes/substituted nitriles	151
CrPCH(SiMe ₃) ₂	alkynes, alkynes/substituted nitriles	151
	isocyanates	157

The main and original way to synthesize 2*H*-azaphosphirenes **17** is by the reaction of an aminocarbene metal complex **19** and a [bis(trimethylsilyl)methylene]halogenophosphane **20** in the presence of an excess of triethylamine, in generally good yields (50-85%) (Scheme 1.14).¹⁴²

Scheme 1.14 Formation of a 2*H*-azaphosphirene complex from an aminocarbene metal complex and [bis(trimethylsilyl)methylene]halogenophosphanes

Another method for generating 2*H*-azaphosphirene complexes **17** is from the reaction of aminocarbene metal complexes **19** and organodichlorophosphanes **21**, in the presence of an excess of triethylamine, resulting in moderate yields (15-30%) (Scheme 1.15).¹⁵⁸ Using this method other bulky substituents at phosphorus can be made including pentamethylcyclopentadienyl (Cp^{*}), triphenylmethyl, and 2,4,6-triisopropylphenyl.¹⁶¹

Scheme 1.15 Formation of a 2*H*-azaphosphirene complex from an aminocarbene metal complex and an organodichlorophosphane

Generating terminal phosphinidenes **4** from 2*H*-azaphosphirenes **17** is useful in the sense that they can be generated at low temperatures. This method can produce W, Mo, and Cr(CO)₅ phosphinidene complexes but the substituents on phosphorus is limited to two very bulky groups (CH(SiMe₃)₂ and Cp*, see Table 1.5).

1.1.5 Generation of electrophilic terminal phosphinidenes via salt metathesis

Another approach to neutral electrophilic phosphinidenes consists of a salt metathesis reaction between an aminodichlorophosphine **22** and Collman's reagent [Na₂Fe(CO)₄] (Scheme 1.16).

Scheme 1.16 Formation of a terminal phosphinidene complex generated from the reaction of an aminodichlorophosphine and Collman's reagent

The reaction of dichlorophosphines and Collman's reagent has been known for almost 30 years. In 1983, Power et. al. showed that dichlorobis(trimethylsilyl)methylphosphine **23** reacts with Collman's reagent to give a diphosphene metal complex **24** (Scheme 1.17).¹⁶²

Scheme 1.17 Reaction of dichlorobis(trimethylsilyl)-methylphosphine and Collman's reagent to form a diphosphene metal complex

A few months later, Cowley et. al. showed that other bulky alkyl dichlorophosphines could also react to give metal complexed diphosphenes.¹⁶³ In that same year, Power et. al. went on to show that the reaction also worked with aminodichlorophosphines (i.e. $\text{PCl}_2\text{N}(\text{SiMe}_3)_2$).¹⁶⁴ In the same article, they also showed that when they changed from $\text{Na}_2\text{Fe}(\text{CO})_4$ to $\text{Na}_2\text{Cr}(\text{CO})_5$ they were able to isolate 3 products (Scheme 1.18). Isolating compounds **25** and **26** containing phosphinidene moieties gave them some insight to what might be going on in the reaction.

Scheme 1.18 Reaction of $\text{PCl}_2\text{N}(\text{SiMe}_3)_2$ with $\text{Na}_2\text{Cr}(\text{CO})_5$

Cowley et. al. on the basis of molecular orbital calculations^{165,166} that revealed significant positive charge accumulation on phosphorus, suggested that terminal phosphinidenes might therefore be stabilized by Lewis base incorporation. In 1987, they successfully isolated a base-stabilized terminal phosphinidene complex **28** using the salt metathesis approach with a dichloro[hydridotris(3,5-dimethyl-1-pyrazolyl)borato]phosphine **27** (Scheme 1.19).¹⁶⁷

Scheme 1.19 Reaction of dichloro[hydridotris(3,5-dimethyl-1-pyrazolyl)borato]phosphine **27** with Collman's reagent to give a base-stabilized terminal phosphinidene complex

Around the same time, King et. al. were attempting to extend the chemistry reactions of Collman's reagent with R_2NPCl_2 derivatives which lead to an array of phosphorus/iron clusters.¹⁶⁸ He suggested that the clusters resulted from the initial formation of the terminal phosphinidene $[R_2N-P \rightarrow Fe(CO)_4]$ followed by dimerization, rearrangement, and CO-loss by several routes.

In 2000, Lammertsma et. al. set out to test if the reaction of aminodichlorophosphines and Collman's reagent in fact generates "free" terminal phosphinidenes, like King had suggested¹⁶⁸ and Cowley's isolated complex inferred¹⁶⁷, and successfully trapped the terminal phosphinidene with allenes¹⁶⁹ and alkynes¹⁷⁰ at -30°C (Scheme 1.16). An extensive list of terminal phosphinidenes generated from this salt metathesis route and their reactions is given in Table 1.6.

Table 1.6 Generation of terminal aminophosphinidenes $[(CO)_4Fe-P-NR_2]$ from the reaction of aminodichlorophosphines and Collman's reagent. Tp* refers to tris(pyrazolyl)borate ligand.

Substituent	Reaction	Reference
FeP(Tp*)	no trapping reagent, intramolecular base stabilization	167
FePN'Pr ₂	allenes	169
	alkynes	170
	1-hexene	75

FePN(ⁱ Pr)(CH ₂) _n CH=CH ₂ , n=1-4	self-condensation, alkynes	171
FePN(CH ₂ CH ₂ CH=CH ₂) ₂	self-condensation, alkynes	171
FePN(ⁱ Pr)(CH ₂) _n C≡C-Me, n=1-2	self-condensation, alkynes	171
FePN(ⁱ Pr)(CH ₂) _n C≡C-Ph, n=3-4	self-condensation, alkynes	171

The benefits of this route are the very low temperatures in which terminal phosphinidenes can be generated (-30°C to rt). The substituents on the phosphorus are limited to bulky secondary amines, and the use of Collman's reagent results in the metal complex being Fe(CO)₄. It should be mentioned that this reaction in the presence of alkenes such as styrene, stilbene, 2,3-dimethyl-1,3-butadiene, 1-methoxy-1-propene, and 1-methoxy-1,3-cyclohexadiene failed to give the corresponding phosphiranes and merely gave the phosphorus/iron cluster.¹⁶⁹ These are substrates that terminal phosphinidenes generated via the 7-phosphanorbornadiene approach (e.g. Ph, Me) do react with. This demonstrates that these terminal phosphinidene complexes are less electrophilic than their tungsten, molybdenum, and chromium counterparts. Without the presence of a substrate these terminal phosphinidenes (i.e. (CO)₄FePN(ⁱPr)₂) form phosphorus/iron clusters.¹⁶⁸

It must be mentioned that very recently (2011), Graham and Carty, using a salt metathesis approach, with an aminodichlorophosphine **22** and Na₂[CpV(CO)₃], were able to synthesize and structurally characterize the first neutral electrophilic terminal phosphinidene complex **29** (Scheme 1.20).¹⁷² It is also the first electrophilic phosphinidene complex of vanadium. Its subsequent reactions with diphenyl acetylene and singlet carbenes substantiate its electrophilic nature.

Scheme 1.20 Generation of the first thermally stable neutral electrophilic phosphinidene complex of vanadium using a salt metathesis reaction. Selected bond lengths and angles of complex **29**: V—P, 2.300(2) Å; P—N, 1.6520(6) Å; V—P—N, 120.65(2)°

1.2 Cationic Electrophilic Phosphinidenes

It should be mentioned that another type of electrophilic phosphinidene exists, where instead of being neutral it is cationic. Whereas the neutral electrophilic phosphinidenes have been generated as transient species and have eluded spectroscopic detection, many cationic electrophilic phosphinidenes have been shown to be stable, isolable, and extremely water-sensitive. These cationic electrophilic phosphinidenes combine the use of electron-donating (i.e. Cp, Cp*, PPh₃) and electron-withdrawing (i.e. CO) ligands, and contain a nitrogen (i.e. π donor) substituent at phosphorus to help stabilize the singlet state, but it is ultimately the cationic charge that ensures that these species act as electrophiles. The main method for their generation will be described below.

1.2.1 Generation of Cationic Electrophilic Phosphinidenes

The main method for generating cationic electrophilic phosphinidenes **31** is from the chloride abstraction of a chloroaminophosphido metal complex **30** (Scheme 1.21). Typically aluminum chloride is used as the Lewis acid, but triphenylmethyl hexafluorophosphate [$\text{C}(\text{C}_6\text{H}_5)_3\text{PF}_6$] has also been used.

Scheme 1.21 Generation of a cationic electrophilic phosphinidene by chloride abstraction

In fact, the first spectroscopic evidence of a terminal phosphinidene complex was achieved using this route. In 1984, Bertrand and Gladysz were able to record the ^{31}P NMR of cationic phosphinidene complex **33** at -90°C (^{31}P NMR = +954).¹⁷³ As the temperature was increased they obtained the C-H insertion product **34** of the phosphinidene into one of the isopropyl hydrogens (Scheme 1.22).

Scheme 1.22 Reaction providing the first spectroscopic evidence of terminal phosphinidenes

Seven years later, in 1991, Niecke et. al. by incorporating bulkier groups on the nitrogen were able to get similar phosphinidene ^{31}P NMR shifts, but this time at room temperature.¹⁷⁴ Finally in 2001, Carty et. al. successfully isolated and structurally characterized stable cationic aminophosphinidene complexes for molybdenum,¹⁷⁵ tungsten,¹⁷⁵ and ruthenium^{175,176} using this approach. They then went on to characterize the iron,¹⁷⁶ osmium,¹⁷⁶ cobalt,¹⁷⁷ and rhenium¹⁷⁸ complexed cationic aminophosphinidenes. The iron aminophosphinidene complex that Carty et. al. isolated¹⁷⁶ in 2003, is of historical significance. It was the same cationic terminal phosphinidene that Bertrand and Gladysz had spectroscopically detected¹⁷³ at low temperatures nearly 20 years earlier, complex **33**, but could not isolate. What Carty et. al. explained was that complex **33** is in fact thermally stable but only under rigorously anhydrous conditions.¹⁷⁶

All the cationic phosphinidene complexes **31** that have been characterized by X-ray crystallography display bent structures with a long P-M bond, and a short P-N bond due to π -donation (Figure 1.5) of the stabilizing amino group into the empty phosphorus p-orbital (e.g. Mo—P, 2.4506(4) Å, P—N, 1.631(1) Å, Mo—P—N, 118.79(5)°;¹⁷⁵ W—P, 2.4503(6) Å, P—N, 1.629(2) Å, W—P—N, 118.69(8)°;¹⁷⁵ Fe—P, 2.151(1) Å, P—N, 1.629(4) Å, Fe—P—N, 118.6(1)°¹⁷⁶).

Figure 1.5 Bonding in electrophilic phosphinidene complexes with an amino group

The reaction of the cationic cobalt complex **31** [$\text{M} = \text{Co}(\text{CO})_3(\text{PPh}_3)$] with diphenylacetylene has been shown to give the [1+2] cycloaddition product (i.e. the

phosphirene complex)¹⁷⁷, showing similar reactivity as its transient neutral electrophilic phosphinidene counterpart $[(\text{CO})_5\text{M} \leftarrow \text{P-R}]$ ($\text{M} = \text{W}, \text{Mo}, \text{Cr}$).¹²⁵

The advantages of this method are that electrophilic phosphinidenes can be generated very easily (i.e. chloride abstraction) at extremely low temperatures (e.g. -90°C). These cationic electrophilic phosphinidenes are stable and isolable (although extremely water sensitive), and can be synthesized with a variety of transition metals. Unfortunately the substituent on the phosphorus is limited to bulky amino groups, usually diisopropylamine. Because this kind of terminal phosphinidene has a strong σ -donor (e.g., Cp) increasing the electron density on phosphorus, and a cationic charge to ensure that the species behaves as an electrophile, it does not always behave as its neutral electrophilic counterpart. For example, the reaction of Carty et. al. molybdenum cationic phosphinidene complex **35** with phenyl acetylene resulted in the [2+2]cycloaddition, to form the phosphametalocyclobutene product **36** (Scheme 1.23).¹⁷⁹

Scheme 1.23 Reaction of the molybdenum cationic phosphinidene complex with phenyl acetylene

Whereas, the reaction of the transient electrophilic phosphinidene complex $[(\text{CO})_5\text{W} \leftarrow \text{PNEt}_2]$ is known to react with phenyl acetylene to give the [1+2]

cycloaddition product, i.e. the complexed phosphirene (see next section, Scheme 1.24).¹³³

Another possibility for stabilizing the singlet state of phosphinidenes is to donate an electron pair (i.e. a lewis base) into the vacant P_y orbital on phosphorus (Fig. 1.1). This donation of electron density causes these species to be nucleophilic at phosphorus and exhibits a different chemistry than that of electrophilic terminal phosphinidenes. A brief section describing these species is included in the appendix.

1.3 Trapping reactions of electrophilic phosphinidene complexes

Terminal phosphinidene complexes have significant potential as synthetic tools in organophosphorus chemistry. Since their discovery¹⁸ in 1982 by Mathey, a plethora of reactions have been reported (see Tables 1.1-1.6) that demonstrate them to be an extremely powerful tool for making new organophosphorus compounds. The following section aims to provide a brief overview of some of the reactions electrophilic phosphinidene complexes undergo. The reaction of these phosphinidene complexes can be classified into five main categories: cycloadditions, insertion into σ -bonds, reactions with nucleophiles, oligomerizations, and rearrangements. The majority of the following reactions were first done using the 7-PNBD approach for generation of the terminal phosphinidene. If an alternative route has been used it shall be indicated.

The first type that will be discussed are cycloaddition reactions. In 1982, Mathey et. al. demonstrated that terminal phosphinidenes **1** react with alkynes to form the [1+2] cycloaddition product, the metal complexed phosphirene **37** (Scheme 1.24), which they also structurally characterized.¹⁸

Scheme 1.24 Reaction of a terminal phosphinidene complex with alkynes to generate phosphirene complexes

This complex is of historical importance, for it was the first phosphirene to be synthesized and structurally characterized. A previous report in 1972, by Stille et. al. of a phosphirene oxide¹⁸⁰ was later shown by Quast et. al. to be incorrect.¹⁸¹ Terminal phosphinidenes can also perform [1+2] cycloaddition reactions with alkenes, to give the corresponding phosphirane complex **38** (Scheme 1.25).²² The stereochemistry of the starting olefin is retained in the phosphirane ring, demonstrating the concerted process.

Scheme 1.25 Reaction of a terminal phosphinidene complex with alkenes to generate phosphirane complexes

They react with conjugated dienes to first give vinylphosphirane complexes **39** around 55°C. Heating at higher temp. (i.e. 100°C) they can thermally rearrange to the phospholene complex **40** (Scheme 1.26).²²

Scheme 1.26 Reaction of a terminal phosphinidene complex with conjugated dienes to give vinylphosphirane complexes, which upon heating can give the phospholene complex

The reaction of terminal phosphinidenes with α,β -unsaturated ketones²² (a.k.a α -enones)(Scheme 1.27) and 1-azadienes¹¹⁰ (Scheme 1.28) results in the [1+4] cycloadduct **41** and **42** respectively. Preliminary formation of the [1+2] adduct with the C=C bond followed by ring expansion cannot be completely ruled out.

Scheme 1.27 Reaction of a terminal phosphinidene complex with α,β -unsaturated ketones

Scheme 1.28 Reaction of a terminal phosphinidene complex with 1-azadienes

Terminal phosphinidenes have also been allowed to react with several double bonds involving heteroatoms. When the substituent on phosphorus is not bulky, and depending on the structure of the carbonyl compound, reactions with ketones can lead to a variety of products.^{42,45} As for terminal phosphinidenes with bulky substituents on phosphorus generated from the 2-azaphosphirene, Streubel et. al. has shown the

reaction undergoes a [1+2] cycloaddition^{143, 149} to form the oxaphosphirane tungsten complex **43** (Scheme 1.29).

Scheme 1.29 Reaction of a terminal phosphinidene complex with an aldehyde giving the oxaphosphirane tungsten complex

Scheme 1.30 Reaction of a terminal phosphinidene complex with an imine giving the azaphosphirane tungsten complex

They also showed that a similar reaction takes place with imines as well to give the corresponding azaphosphirane (or azaphosphiridine) tungsten complex **44** (Scheme 1.30).¹⁴⁹ With ordinary substituents, the reaction is more complex and gives a variety of four- and five-membered rings, likely resulting from insertion of either one molecule of imine or one molecule of phosphinidene into the weak P-N bond of the initially formed [1+2] cycloadduct, the azaphosphirane (Scheme 1.31).⁴⁹

Scheme 1.31 Reaction of a methylphosphinidene tungsten complex with *N*-methyl(benzylidene)amine

Terminal phosphinidenes also undergo [1+2] cycloadditions with silenes⁵⁵ (Scheme 1.32) and phosphalkenes³⁹ (Scheme 1.33). In the case of the reaction with phosphalkenes, the diphosphirane product **45** spontaneously loses its complexing group.

Scheme 1.32 Reaction of a terminal phosphinidene and a silene

Scheme 1.33 Reaction of a terminal phosphinidene and a phosphalkene

Even hetero-triple bonds have been used in similar [1+2] cycloaddition reactions. The condensation reaction of an aminophosphinidene complex with *tert*-butylphosphacetylene (Scheme 1.34) gives diphosphirene complex **46**, which then over time can undergo a series of transformations resulting in complex **47**.¹³⁴

Scheme 1.34 Reaction of a terminal phosphinidene and a phosphalkyne

These [1+2] cycloadditions have also been transposed with various transition metal double bonds. Terminal phosphinidenes react with carbenes^{28,30} to give a formal phosphinidene-carbene coupling product **49** (Scheme 1.35). The transient metallaphosphirane **48** is likely produced, followed by spontaneous loss of $W(CO)_5$ to give the final product.

Scheme 1.35 Reaction of a terminal phosphinidene and a carbene

The transposition with $M=M$ double bonds also works, although in this case, the initial three-membered ring can be characterized (Scheme 1.36).⁸⁸

Scheme 1.36 Reaction of a terminal phosphinidene and a $M=M$ double bond

Reaction with $M\equiv C$ triple bonds has also been investigated. The reaction of a terminal phosphinidene with a carbyne complex gives the expected metallaphosphirene (Scheme 1.37).³²

Scheme 1.37 Reaction of a terminal phosphinidene and a $M\equiv C$ triple bond

It must also be mentioned that the occurrence of [1+2+2] cycloadditions are possible with electron-rich alkenes²² (Scheme 1.38) and alkynes³³ (Scheme 1.39).

Scheme 1.38 Reaction of a terminal phosphinidene and an electron-rich alkene

Scheme 1.39 Reaction of a terminal phosphinidene and an electron-rich alkyne

Another type of reaction that terminal phosphinidenes can undergo is the insertion into σ -bonds. They are known to formally insert into O-H and N-H σ -bonds. Water, unhindered alcohols, and both primary and secondary amines efficiently trap them, resulting in the hydrogen insertion product **51** (Scheme 1.40).

Scheme 1.40 Reaction of a terminal phosphinidene with substrates containing O-H and N-H bonds

The complexing group stabilizes the final product **51**, which is generally unstable in the free state, and has led to many new phosphine complexes. All these formal insertion

reactions are, very likely, driven by an initial attack of the trapping reagent at phosphorus, followed by a hydrogen transfer.

In some cases it is possible to isolate the initial adduct formed, as shown by the reaction with tertiary phosphines (IUPAC recommended name phosphanes) (Scheme 1.41).³⁴ One such adduct ($R = \text{CO}_2\text{Et}$, $R' = \text{Et}$) has been characterized by X-ray analysis.

Scheme 1.41 Reaction of a terminal phosphinidene with tertiary phosphines

These phosphaylid complexes **52** can react cleanly with carbonyl compounds to give phosphalkene complexes **53** via a “phospha-Wittig” reaction (Scheme 1.42).³⁴

Scheme 1.42 The “phospha-Wittig” reaction: reaction of a phosphaylid with a carbonyl compound to give a phosphalkene complex

As we have seen earlier from the work of Bertrand and Gladysz (Scheme 1.22), phosphinidenes have been shown to undergo intramolecular C-H insertion.¹⁷³ The first intermolecular C-H bond insertion was shown by Mathey et. al. with the successful insertion of a terminal phosphinidene into the C-H bond in ferrocene (Scheme 1.43).²⁷

Scheme 1.43 Insertion of a terminal phosphinidene into the C-H bond of ferrocene

Another type of insertion reaction into σ -bonds occurs with strained 3-membered heterocycles. With aziridines **54**, stable four-membered rings **55** are obtained (Scheme 1.44).²⁹

Scheme 1.44 Insertion of a terminal phosphinidene into the P-N bond of aziridines

They also insert in the P-C σ -bond of 2-alkynylphosphirenes **56** (Scheme 1.45).^{47,52} The conjugation of the 2-alkynyl substituent destabilizes the P-C(2) bond of the phosphirene ring. Without this substituent, no phosphinidene insertion is observed. Also the insertion into a transition metal M-C bond has been described. Terminal phosphinidenes have been shown to insert into a Ni-C bond (Scheme 1.46).⁸⁶

Scheme 1.45 Insertion of a terminal phosphinidene into the P-C bond of a 2-alkynylphosphirene tungsten complex

Scheme 1.46 Insertion of a terminal phosphinidene into a Ni-C bond

When terminal phosphinidenes are generated in the absence of a trapping reagent they can form oligomers. In the presence of CuCl, dimers^{20,46,93} can be formed (Scheme. 1.47). Both theoretical and experimental evidence supports the fact that the copper chloride remains coordinated to the expelled phosphinidene.^{11,60,94,95} It has been suggested that two phosphinidenes in the coordination sphere of copper could undergo oxidative coupling, followed by reductive elimination of the copper to form the P=P double bond.⁹³

Scheme 1.47 Dimerization of a terminal phosphinidene in the presence of CuCl

Without CuCl, terminal phosphinidenes can react to form either trimers (Scheme 1.48) or tetramers (Scheme 1.49) depending on the conditions.⁴⁶

Scheme 1.48 Trimerization of a terminal phosphinidene

Scheme 1.49 Tetramerization of a terminal phosphinidene

Terminal phosphinidenes can also undergo intramolecular rearrangement with the appropriate functional group. One example of this is the chloromethylphosphinidene tungsten complex **57**. When the terminal phosphinidene **57** is generated in the presence of CuCl, it rearranges to the corresponding chlorophosphaalkene π -complex **58** (Scheme 1.50).^{94,95}

Scheme 1.50 Chloromethylphosphinidene tungsten complex undergoing an intramolecular rearrangement with CuCl to give the chlorophosphaalkene π -complex

With their general ease of synthesis, large range of substituents, and an impressive array of reactions with organic and organometallic molecules, electrophilic phosphinidenes are a powerful synthetic tool in organophosphorus chemistry. Their reactions with substrates has led to many new and exciting organophosphorus compounds, e.g. the 3-membered phosphirene ring. However, to be truly effective, their chemistry needs to be coupled with efficient decomplexation techniques. The following section will describe the techniques for decomplexing the metal from phosphorus.

1.4 Decomplexation techniques for removing transition metals from phosphorus

The choice of complexing group (i.e. ML_n) is useful in tuning the electrophilicity and the lifetime of the phosphinidene moiety, as well as the stability of the reaction product. But if the final synthetic products are ligands or bioactive molecules, the complexing group must be removed. The majority of work done so far with electrophilic phosphinidenes uses the 7-PNBD route as the generation technique, which incorporates pentacarbonyl group VI transition metal centers as the complexing group. In practice, the most effective complexing group is the tungsten pentacarbonyl unit, as this is the one that gives the strongest bond to the phosphorus atom. This section aims to provide an overview of common decomplexing techniques for tungsten (as well as other group VI) transition metal centers.

1.4.1 Oxidation of tungsten followed by ligand exchange

The first, and oldest technique, involves an oxidation of W^0 to W^{II} by I_2 , which weakens the P-W bond, followed by a displacement of the phosphorus ligand by 1-methylimidazole **59** at room temperature.^{182,44,183} Using this technique, the first trivalent phosphirene **60** was isolated and structurally characterized (Scheme 1.51) by Mathey et. al. in 1984.¹⁸²

Scheme 1.51 An example of the oxidation/ligand exchange technique for removal of tungsten using I_2 and 1-methylimidazole¹⁸²

A variation of this technique incorporates pyridinium tribromide ($\text{PhNMe}_3^+ \text{Br}_3^-$ has also been used) as the halogenation reagent and 2,2'-bipyridine as the ligand for displacement (Scheme 1.52 and 1.53).^{117,184}

Scheme 1.52 Oxidation/ligand exchange technique for removal of tungsten using pyridinium tribromide and 2,2'-bipyridine¹¹⁷

Scheme 1.53 Oxidation/ligand exchange technique for removal of tungsten from a chlorophosphirene¹⁸⁴

1.4.2 Direct exchange

Due to the fact that the previous method suffered from the potential for oxidizing the trivalent phosphorus center (Scheme 1.52) another method was proposed. This new method relies on the displacement of the phosphorus ligand by a chelating bidentate diphosphene ligand such as 1,2-bis(diphenylphosphino)ethane **63** (or dppe) (Scheme 1.54 and 1.55).^{185,99,135} This technique can only be applied for the displacement of monodentate ligands, and works for molybdenum¹⁸⁵ as well. As can be seen from the

examples, the temperature and reaction times vary depending on the monodentate ligand.

Scheme 1.54 Direct exchange technique for removal of tungsten from a chlorophosphirene¹³⁵

Scheme 1.55 Direct exchange technique for removal of tungsten from a tetra-substituted phosphole⁹⁹

1.4.3 Oxidative decomplexation

The next method involves removal of the transition metal under oxidative conditions. It turns out that trimethylamine oxide (Me_3NO) is the reagent of choice for the conversion of the $[P-W(CO)_5]$, $[P-Mo(CO)_5]$, or $[Fe(CO)_4]$ complexes into their corresponding phosphorus oxides (Scheme 1.56 and 1.57).^{186,59}

Scheme 1.56 Oxidation decomplexation of a tricyclic system containing two phospholene tungsten complexes using trimethylamine oxide¹⁸⁶

Scheme 1.57 Oxidation decomplexation of a phosphinite tungsten complex using trimethylamine oxide⁵⁹

Specifically for [P-Mo(CO)₅] complexes, another possible oxidation decomplexation reaction uses sulfur as a mild oxidation method, to give the corresponding phosphorus sulfides (Scheme 1.58).¹⁸⁷

Scheme 1.58 Oxidation decomplexation of a phospholene molybdenum complex using sulfur

1.4.4 Electrochemical decomplexation

In 2004, Mathey et. al. discovered a new way to decomplex [P-W(CO)₅], by electrochemical reduction. In a preparative electrochemical cell, under argon, they were able to perform 2e reductions of tungsten on a variety of substituted phosphole complexes (Scheme 1.59).¹⁸⁸ In the case where R = Ph the isolated yield of the product was 84%.

Scheme 1.59 Electrochemical reduction of tungsten as a method for decomplexation

1.4.5 Decomplexation by weakening of P-M bond and applying CO pressure

In 2006, Lammertsma et. al. discovered a new method for decomplexing molybdenum from phosphirenes and phosphirane complexes (Scheme 1.60).¹²³ This method replaces one CO ligand on molybdenum for a trimethylphosphine ligand, which weakens the phosphirene P-Mo bond. Next, by applying CO pressure they are able to decomplex the phosphirene or phosphirane from the metal.

Scheme 1.60 Decomplexation of molybdenum by replacing one CO with PMe₃ and applying CO pressure

The phosphirene and phosphirane molybdenum complexes used in this method are synthesized from the reaction of phosphinidene **64** with alkynes and alkenes (Scheme 1.61).

Scheme 1.61 Generation of the phosphinidene to be used for the weakened P-Mo bond/CO pressure method for decomplexation

1.5 Conclusion

The majority of organophosphorus chemistry is constructed around P(III) and P(V) oxidation states. What many organophosphorus chemists have been attempting to do for some time is to incorporate and develop the chemistry of the P(I) oxidation state. Early attempts to develop the naturally unstable phosphinidenes [R-P] were not so fruitful due to their unpredictable chemistry. The root of the problem lies with the fact that phosphinidenes have a triplet ground state with a huge triplet-singlet gap. In 1982, Mathey et. al. discovered a solution to this problem. By complexing one of the lone pairs of the phosphinidene [R-P] to a transition metal (M = W, Mo, Cr), they could generate terminal phosphinidenes [R-P-M(CO)₅] that have a singlet ground state and could display a reactivity that closely resembles that of singlet carbenes.

To date there are 5 main ways to generate these transient electrophilic species. They can be generated with a variety of substituents on phosphorus, and undergo an impressive array of reactions with organic and organometallic molecules to give many new and exciting organophosphorus compounds. If desired, these compounds can then be decomplexed by several methods to give the “free” trivalent-phosphorus species, which can later be used as ligands for catalysis or as bioactive molecules.

But the quest for expanding the chemistry of monovalent phosphorus P(I) is not over. By incorporating new substituents on phosphorus, or by finding new substrates with which to trap the terminal phosphinidenes, paths for finding new organophosphorus compounds can be discovered. As one travels down these paths, one realizes that there is still plenty waiting to be discovered.

The following chapters will discuss my journey of developing the chemistry of monovalent phosphorus and the discoveries that happened along the way.

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CHAPTER 2

Generation and Trapping of a Terminal Chlorophosphinidene Complex

2.1 Introduction

A large amount of work has recently been devoted to the chemistry of terminal phosphinidene complexes.¹ Just as for carbene complexes, terminal phosphinidenes exist in two varieties: the nucleophilic type, which displays a phospho-Wittig reactivity, and the electrophilic type, which displays a reactivity similar to that of singlet carbenes. Within this last group, the transient group VI transition metal pentacarbonyl complexes $[(CO)_5M \leftarrow P-R]$, are the most studied and the most useful. If one examines the extensive list of phosphinidene complexes, one finds that the halophosphinidene complexes $[(CO)_5M \leftarrow P-X]$ are noticeably absent. This absence is surprising since they would combine a higher electrophilicity than the alkyl or aryl species with the additional synthetic potential of the P-X bond.

Preliminary work of fluorophosphinidene complexes yielded mixed results. In 1986, Mathey et. al. synthesized the 7-fluoro-7-phosphanorbornadiene tungsten complex **66** (Scheme 2.1).²

Scheme 2.1 Synthesis of the 7-fluoro-7-phosphanorbornadiene tungsten complex

Unfortunately complex **66** appeared to be too stable and was not able to generate the fluorophosphinidene complex **67**, even at 160°C for 7 hours in the presence of CuCl as a catalyst and diphenyl acetylene as a trapping agent (Scheme 2.2).

Scheme 2.2 Heating of the 7-fluoro-7-phosphanorbornadiene tungsten complex does not yield the fluorophosphinidene tungsten complex

The fluorine substituent drastically enhanced the stability of the 7-phosphanorbornadiene, preventing the bridge from collapsing and generating the fluorophosphinidene complex **67**. They reasoned that a stronger P-M bond was also likely to introduce a stronger stabilization of the phosphorus ligand. For example, it is known that in the $[R_3P \rightarrow M(CO)_5]$ series, the P-M bond dissociation energies always vary in the following order $P-W > P-Cr > P-Mo$.³ Thus because they wanted to make a less stable 7-phosphanorbornadiene, they sought to investigate the synthesis and subsequent thermal decomposition of a 7-fluoro-7-phosphanorbornadiene molybdenum complex. In 2006, twenty years later, Mathey et. al. were able to synthesize the 7-fluoro-7-phosphanorbornadiene molybdenum complex **68** (Scheme 2.3).⁴

Scheme 2.3 Synthesis of the 7-fluoro-7-phosphanorbornadiene molybdenum complex

They were then able to generate the fluorophosphinidene molybdenum complex at 120°C and trap it with diphenyl acetylene and 2,3-dimethylbutadiene (Scheme 2.4).

Scheme 2.4 Trapping reactions of a fluorophosphinidene molybdenum complex

Unfortunately at 120°C, these conditions are still a bit too drastic for many trapping reactions. Thus we decided to reinvestigate this problem more in depth.

2.2 Results and discussion

We first performed comparative DFT calculations⁵ on $[(CO)_5Cr-P-F]$, $[(CO)_5Cr-P-Cl]$, and $[(CO)_5Cr-P-Me]$ at the B3LYP/6-31G(d)-lanl2dz(Cr) level.^{6,7} The results were a little surprising. The NBO charge at phosphorus is calculated to be lower for Cl (+0.55e) than for Me (+0.60e) and F (+0.94e). This would suggest that there is a strong interaction between the lone pairs on chlorine and the vacancy at phosphorus in $[(CO)_5Cr-P-Cl]$, as was confirmed by the shapes of the HOMO and LUMO (Figure 2.1).

Figure 2.1 HOMO and LUMO of $[(\text{CO})_5\text{Cr-P-Cl}]$

The σ lone pair, coming out of the plane of the paper at phosphorus, (HOMO) is stabilized (i.e. positive overlap) by the interaction with chlorine, whereas the empty p_z orbital at P, in the plane of the paper, (LUMO) is destabilized. Because the P-Cl bond is long⁸ (2.107 Å) this destabilization is weak. In the case of the fluorophosphinidene, the destabilization is much stronger because the P-F bond is short (1.632 Å). This causes the LUMO of $[(\text{CO})_5\text{Cr-P-F}]$ to rise in energy, so as to be at the same level as the LUMO of $[(\text{CO})_5\text{Cr-P-Me}]$. This results in the levels of the HOMOs and LUMOs to be perturbed differently in $[(\text{CO})_5\text{Cr-P-Cl}]$ and $[(\text{CO})_5\text{Cr-P-F}]$ when compared to $[(\text{CO})_5\text{Cr-P-Me}]$ (see Figure 2.2).

The unexpected predictions of these computations suggest that the chlorophosphinidene complex would behave as the most electrophilic of the three species, since its LUMO is significantly lower in energy than the other two (Figure 2.2). With this new information in mind we sought out to pursue the generation of the very electrophilic chlorophosphinidene.

As we have seen in Chapter 1, there are five ways of generating terminal phosphinidenes: the 7-phosphanorbornadiene,⁹ phosphirane,¹⁰ phosphepine,¹¹ azaphosphirene,¹² and salt metathesis¹³ methods. The salt metathesis method works by incorporating bulky amino substituents on the phosphorus, thus not a suitable candidate. Both the phosphepine and the azaphosphirene methods are difficult to imagine for the synthesis of the chlorophosphinidene complexes, based on the starting reagents needed for the synthesis of the precursors. And as we have seen, the phosphirane method works best when the phosphorus has an amino substituent. Thus we are left with the original 7-phosphanorbornadiene route. The starting point must be the 1-chloro-3,4-dimethylphosphole tungsten complex **70**. This complex is known² but delicate to prepare due to the use of SO_2Cl_2 , and its tendency to oxidize tungsten. Because the reproducibility of this complex was rather low, Mathey et. al. discontinued its use and began investigating the replacement of the chlorine with other electronegative substituents (e.g. $-\text{CO}_2\text{Et}$, and $-\text{CN}$).¹⁴ Thus we first needed a new method of synthesis for the 1-chloro-3,4-dimethylphosphole tungsten complex **70**. The new method is depicted below (Scheme 2.5).

Scheme 2.5 Synthesis of 1-chloro-3,4-dimethylphosphole pentacarbonyltungsten

In addition to the previously reported characterizations of the 1-chlorophosphole complex **70**,² we have recorded its ^{13}C NMR spectrum and performed an X-ray crystal structure analysis (Figure 2.3).

Figure 2.3 X-ray crystal structure of 1-chloro-2,3-dimethylphosphole tungsten pentacarbonyl complex. Selected bond lengths (Å) and angles (deg): P1–W1 2.4516(8), P1–Cl1 2.0546(13), P1–C1 1.772(3), P1–C4 1.783(4), C1–C2 1.331(5), C2–C3 1.476(5), C3–C4 1.332(5); C1–P1–Cl1 101.66(13)°, C4–P1–Cl1 103.85(15)°, C1–P1–C4 91.24(17)°, C1–P1–W1 123.22(12)°, C4–P1–W1 118.84(13)°, Cl1–P1–W1 114.13(5)°.

Ellipsoids drawn at 50% probability level.

Care must be taken with the addition of the phospholide tungsten complex **69** to C_2Cl_6 . The addition must be done slowly with excess C_2Cl_6 to minimize the reaction of the phospholide tungsten complex **69** with the newly formed 1-chlorophosphole tungsten

complex **70** to give the 1,1'-biphosphole bistungsten complex **71** (Scheme 2.6). The formation of 1,1'-biphosphole bistungsten complex **71** can never be completely avoided, thus a small amount is always present in the crude mixture. Upon column chromatography, the biposphole complex **71** is destroyed and the chlorophosphole complex **70** is isolated. Complex **71** has previously been described.¹⁵

Scheme 2.6 Formation of the 1,1'-biphosphole bistungsten complex

Previously when Mathey et. al. synthesized the chlorophosphole complex **70**, they attempted to react it with dimethyl acetylenedicarboxylate (DMAD) to form the 7-chloro-7-phosphanorbornadiene tungsten complex **72**, but all their attempts failed.² Nevertheless, we decided to perform the reaction again, but this time carefully monitoring the reaction in toluene by ³¹P NMR. We discovered that, at 60°C, the reaction proceeds slowly to give the expected 7-phosphanorbornadiene complex with its characteristic low-field shift: $\delta^{31\text{P}} = +187.2$. The peak reaches a maximum after ca. 11-12 hours, but the decomposition starts before all of the starting 1-chlorophosphole complex **70** has been consumed (Scheme 2.7). At 75°C, the 7-phosphanorbornadiene has been generated and subsequently completely destroyed within ca. 5 hours.

Scheme 2.7 Formation of the 7-chloro-7-phosphanorbornadiene tungsten complex and its subsequent decomposition at approximately the same temperature

It is interesting to note that the 7-chloro-7-phosphanorbornadiene tungsten complex is both generated and destroyed within several hours around 60-75°C. The 7-phosphanorbornadiene tungsten complexes usually require higher temperatures and longer reaction times to be generated, from the reaction of the corresponding phosphole complex with DMAD (e.g. R=Me with DMAD, 85-90°C for 15h; R=Ph with DMAD, 85-90°C for 24h).¹⁶ They also decompose and generate the terminal phosphinidenes to react with substrates at much higher temperatures (e.g. R=Ph 115°C for 5 hours with trans-stillbene, or 115°C for 7 hours with cyclooctene).¹⁷ Thus, it may be for this reason why Mathey et. al. previous reactions of 1-chlorophosphole tungsten complex **70** and DMAD had failed. Merely, the temperature of generation and decomposition of the 7-chloro-7-phosphanorbornadiene tungsten complex was much lower than what was expected. If one were to heat the 1-chlorophosphole tungsten complex **70** with DMAD at too high a temperature all one would see is decomposition by ³¹P NMR.

If we could isolate the 7-chloro-7-phosphanorbornadiene tungsten complex **72** we could have a “clean” precursor of the chlorophosphinidene. Unfortunately, our attempts to push the reaction toward a maximum of the 7-chlorophosphanorbornadiene and subsequently try to isolate it were unsuccessful.

It seemed as if we were missing the right technique to accomplish this task. A point we never forgot about and will return to later on.

As was mentioned in chapter 1, if the 7-phosphanorbornadiene complex is too reactive or displays too low a stability (e.g. $R = \text{CN}^{14}$, $R = \text{C}\equiv\text{C-Ph}^{18}$, or $M = \text{Fe}(\text{CO})_4^{19}$) it is possible to add the mixture of phosphole complex, the dimethyl acetylenedicarboxylate (DMAD), and the substrate, to trap the phosphinidene as soon as it is generated. Thus, we next performed the reaction with the mixture of 1-chlorophosphole complex **70**, DMAD, and diphenylacetylene, in a one-pot reaction and successfully trapped the chlorophosphinidene complex **73** (Scheme 2.8). The chlorophosphirene complex **74** has been described already by another method.²⁰ This experiment convincingly demonstrated that the chlorophosphole complex **70** and DMAD can be used as a precursor for $[(\text{CO})_5\text{W}\leftarrow\text{P-Cl}]$.

Scheme 2.8 The one-pot reaction for the generation and trapping of a chlorophosphinidene complex with diphenyl acetylene

Next a similar reaction was carried out with cyclohexene as the substrate (Scheme 2.9).

The resulting chlorophosphirane complex **75** was isolated and characterized by X-ray crystal structure analysis (Figure 2.4).

Scheme 2.9 The one-pot reaction for the generation and trapping of a chlorophosphinidene complex with cyclohexene

Figure 2.4 X-ray crystal structure of chlorophosphirane complex **75**. Selected bond lengths (Å) and angles (deg): P1–W1 2.4788(10), P1–Cl1 2.0534(14), P1–C6 1.813(4), P1–C7 1.825(4), C6–C7 1.536(5); C6–P1–C7 49.93(17)°, C6–P1–Cl1 102.14(13)°, C7–P1–Cl1 103.45(14)°, C6–P1–W1 134.15(12)°, C7–P1–W1 133.63(13)°, Cl1–P1–W1 115.97(5)°. Ellipsoids drawn at 50% probability level.

It is interesting to note that the reaction of $[(\text{CO})_5\text{W-P-Ph}]$ with cyclohexene gives the expected nonseparable mixture of isomers with the cyclohexane ring either *cis* or *trans*

to tungsten,²¹ and in this instance to find almost exclusively the more hindered *cis* isomer is obtained.

A problem that can arise from using the one-pot method for generating and trapping terminal phosphinidenes is that sometimes a substrate (i.e. trapping reagent) is also able to react with DMAD. Thus now competing reactions are taking place (i.e. the phosphole and DMAD as well as the substrate and DMAD) and it might prove difficult to trap the terminal phosphinidene, whose concentration in the reaction medium would be very low. But in fact, this is not the case with $[(\text{CO})_5\text{W-P-Cl}]$. The reaction of 1-chlorophosphole complex **70**, with excess DMAD, and excess 2,3-dimethyl butadiene, was carried out at 70°C for 16h in toluene. Monitoring the reaction by ^{31}P NMR, we were able to detect the two expected chlorophosphirane isomers **75a,b** ($\delta^{31}\text{P} = -64.5$ and -58.8) and their rearrangement into the chlorophospholene **76** (Scheme 2.10). The simultaneous competing reaction of the 2,3-dimethyl butadiene with dimethyl acetylenedicarboxylate can be seen in scheme 2.11. It should be mentioned that the uncomplexed chlorophospholene has previously been described.²²

Scheme 2.10 The one-pot reaction for the generation and trapping of a chlorophosphinidene complex with 2,3-dimethyl butadiene

Scheme 2.11 The competing [4+2] reaction of 2,3-dimethyl butadiene with dimethyl acetylenedicarboxylate

The preceding work was published in 2009 in the Journal of the American Chemical Society.²³ The following section includes unpublished results as well as some preliminary experiments, which may lead to future developments.

At the same time we were looking at the reaction of 1-chlorophosphole complex **70** with electron deficient alkynes (i.e. DMAD) we also looked at its reaction with electron deficient alkenes as well. The chlorophosphole complex **70** reacts cleanly with *N*-phenylmaleimide to give the 7-chlorophosphanorbornene **77** (Scheme 2.12). It was characterized by X-ray crystal structure analysis (Figure 2.5). The isolation and characterization of complex **77** demonstrates the increased stability of 7-phosphanorbornene complexes compared to 7-phosphanorbornadiene complexes.

Scheme 2.12 The [4+2] reaction of 1-chlorophosphole complex with *N*-phenylmaleimide

Figure 2.5 X-ray crystal structure of 7-chlorophosphanorbornene tungsten complex **77**.

Selected bond lengths (Å) and angles (deg): P1–W1 2.4479(3), P1–Cl1 2.0832(4), P1–C11 1.8546(12), P1–C6 1.8533(11), C6–C7 1.5223(16), C7–C10 1.3515(16), C10–C11 1.5232(15), C11–C12 1.5520(15), C12–C13 1.5441(16); W1–P1–Cl1 110.133(15)°, C6–P1–C11 81.66(5)°, C6–P1–W1 128.10(4)°, C11–P1–W1 124.26(4)°, C6–P1–Cl1 103.49(4)°, C11–P1–Cl1 104.40(4)° Ellipsoids drawn at 50% probability level.

As we have seen, having chlorine as a substituent on the 7-phosphanorbornadiene tungsten complex dramatically decreased its stability, leading to its decomposition and generation of the chlorophosphinidene **73**. Could it also decrease the stability of the 7-phosphanorbornene tungsten complex **77**? Unfortunately preliminary attempts to collapse the bridge of the 7-chloro-7-phosphanorbornene complex **77** were unsuccessful. Heating of the 7-chloro-7-phosphanorbornene complex **77** with and without the presence of CuCl, in the presence of diphenyl acetylene, at temperatures up to 120°C for 15h did not yield the chlorophosphirene complex **74**. Neither did UV reactions with and without CuCl in the presence of diphenyl acetylene. Though this could be seen as understandable due to the fact that the decomposition of the 7-phosphanorbornene would result in a non-aromatic byproduct (Figure 2.6), and would lack the aromatic character that the phthalate **3** possesses as a driving force for the generation of the phosphinidene.

Figure 2.6 Theoretical non-aromatic byproduct if 7-phosphanorbornene complex **77** were to collapse

Around the same time, Tian and Mathey were investigating the quaternization of uncomplexed 7-phosphanorbornenes to facilitate the collapse of their phosphorus bridge.²⁴ We wondered if we too could introduce something to destabilize the 7-phosphanorbornene complex into collapsing. Initially we tried tetra-*n*-butylammonium fluoride (TBAF) as a source of F⁻, as, Compain and Mathey previously had success using the fluoride ion to collapse the 7-phosphanorbornadiene tungsten complex under mild conditions.²⁵ Unfortunately, in the case of the 7-phosphanorbornene complex **77** only a substitution reaction occurred with the replacement of chlorine with fluorine.

Scheme 2.13 Reaction of the 7-chloro-7-phosphanorbornene with TBAF to give the 7-fluoro-7-phosphanorbornene complex

Another reagent we decided to try was *N*-methylimidazole. In 2006, Kalinina and Mathey had shown that *N*-methylimidazole was able to facilitate the breaking of the 7-phosphanorbornadiene molybdenum complex (Scheme 2.14). They explain that the proposed intermediate **79** is no longer electrophilic at phosphorus but nucleophilic. It

should also be mentioned that Cowley was able to isolate a base-stabilized phosphinidene complex.²⁶

Scheme 2.14 Facilitation of *N*-methylimidazole in breaking the phosphorus bridge for 7-phosphanorbornadiene molybdenum complexes

When we reacted the 7-chloro-7-phosphanorbornene complex **77** with *N*-methylimidazole at 50°C for 12 hours, we quantitatively, by ³¹P NMR, obtained a deep red complex **80** (Scheme 2.15). Unfortunately, preliminary attempts to isolate this complex were unsuccessful. Thus, more work needs to be done to isolate and definitively characterize this complex, as well as, to look into its reactivity. For if complex **80** is similar to Kalinina and Mathey's intermediate **79**, it could be a source of a nucleophilic phosphinidene with the additional synthetic potential of the P–X bond, as opposed to the bulky alkyl or aryl substituents typically used.

Scheme 2.15 Reaction of 7-chloro-7-phosphanorbornene complex with *N*-methylimidazole

We also decided to have a closer look at the chlorophosphirane complex **75**. As we have seen in chapter 1, phosphiranes can be used as precursors for terminal phosphinidenes. Mathey et. al. had previously shown that a phenylphosphinidene $[(CO)_5W-P-Ph]$ could be generated from a phosphirane at $150^\circ C$.¹⁷ But when the substituent was changed to an amino substituent, they could generate the aminophosphinidene from phosphiranes at $70-90^\circ C$.¹⁰ Could the chlorine substituent also have the same effect? Indeed it does. Heating the chlorophosphirane **75** generated the chlorophosphinidene **73**, with loss of cyclohexene, and then was subsequently trapped with diphenyl acetylene to give complex **74** (Scheme 2.16). Thus the chlorophosphirane complex **75** is a “clean” precursor for the generation of chlorophosphinidene **73**. Another additional bonus is that the byproduct, cyclohexene, is a low boiling liquid, which can easily be removed by evaporation under vacuum, thus simplifying purification. This is because occasionally if the final product from the trapping reaction of the terminal phosphinidene is polar, then the phthalate **3**, the byproduct of the 7-phosphanorbornadiene method, can sometimes elute together with the product, making the purification and isolation difficult. If the product is non-polar, separation from the phthalate **3** is not a problem.

Scheme 2.16 Generation of chlorophosphinidene from a chlorophosphirane complex with subsequent trapping with diphenyl acetylene

The following reaction is an example where using the chlorophosphirane complex **75**, as the precursor for the chlorophosphinidene **73**, can be beneficial instead of the chlorophosphole **70**/DMAD approach. In the one-pot reaction of chlorophosphole **70**, DMAD, and trimethylsilylacetylene, the final product, the chlorophosphirane **81**, could be detected by ^{31}P NMR (Scheme 2.17). But as the reaction proceeded the reaction mixture became thicker and more viscous to the point where stirring became difficult. It appeared that side reactions were taking place with the DMAD and/or the trimethylsilylacetylene forming an insoluble polymeric-type product, making the reaction and isolation of the product more difficult. Cyclotrimerization and polymerization of alkynes in the presence of group VI metallic centers is known.²⁷ Polymerization of the alkynes in the reaction medium is most likely taking place in the coordination sphere of trace amounts of tungsten.

Scheme 2.17 One pot reaction of the chlorophosphole complex with dimethyl acetylenedicarboxylate to generate the chlorophosphinidene and its subsequent trapping with trimethylsilylacetylene

Next we tried the reaction using the chlorophosphirane **75** as the source of chlorophosphinidene **73** and reacted it with trimethylsilylacetylene. The reaction proceeded cleanly with a shorter reaction time and in a much higher yield (Scheme 2.18). Some insoluble polymeric-type substance was still detected suggesting that the trimethylsilylacetylene is reacting with itself at the elevated temperatures.

Scheme 2.18 Generation of the chlorophosphinidene from the chlorophosphirane complex and its subsequent trapping with trimethylsilylacetylene

Using this method, we also trapped the chlorophosphinidene complex **73** with styrene to yield two isomers **82a,b** in high yield (Scheme 2.19).

Scheme 2.19 Generation of the chlorophosphinidene from the chlorophosphirane complex and its subsequent trapping with styrene

Previously, Mathey et. al. had shown that terminal phosphinidenes generated by their respective 7-phosphanorbornadienes were able to insert into the electron rich C-H bond of ferrocene.²⁸ Based on the comparative DFT calculations we performed, the chlorophosphinidene complex **73** should be the most electrophilic of the terminal phosphinidenes. Thus it too should have no problem performing an intermolecular insertion into the ferrocene C-H bond. We performed the one-pot reaction of 1-chlorophosphole complex **70** with DMAD and ferrocene at 75°C and to our disappointment only decomposition (i.e. a drastic decrease in signal-to-noise ratio making it difficult to distinguish the presence of products) was observed (Scheme 2.20).

Scheme 2.20 Unsuccessful attempt to trap the chlorophosphinidene into the C-H bond of ferrocene using the one-pot approach

Due to the fact that occasional side reactions can occur using the one-pot approach for generation of the phosphinidene, we performed the reaction again using the chlorophosphirane complex **75** and to our surprise it too also resulted in mainly decomposition.

Scheme 2.21 Unsuccessful attempt to trap the chlorophosphinidene into the C-H bond of ferrocene from the chlorophosphirane complex

Mathey et. al. were previously able to perform the C-H insertion, but the chlorophosphinidene, which should be the most electrophilic, is not able to. This result was an anomaly. We decided to go back to the literature and thoroughly examine what could be missing. One thing stood out, and it was the fact that all the successful intermolecular insertion reactions into the C-H bond of ferrocene, incorporated the use of CuCl as a catalyst for breaking the 7-phosphanorbornadiene bridge. As mentioned in chapter 1, in some instances the use of CuCl can alter the course of the reaction. Lammertsma's DFT calculations²⁹, as well as experimental evidence³⁰, suggest that

when CuCl is used as a catalyst to facilitate the breaking of the 7-phosphanorbornadiene bridge, the intermediate is not a free terminal phosphinidene $[(CO)_5W-P-R]$ but a phosphinidenoid complex $[W(CO)_5(RP(Cu-L)Cl)]$ **5**.²⁹ And it is this phosphinidenoid complex, that for the most part, reacts similar to a free terminal phosphinidene but can occasionally undergo an alternate reaction course.^{31,32,1g,29,33,30,34,35} The question is, is this one of those instances where the phosphinidenoid complex is necessary for the insertion of the phosphinidene into the ferrocene C-H bond?

To test this, we tried the reaction of the chlorophosphinidene again with ferrocene, but this time in the presence of CuCl. This time, the reaction was successful in giving the corresponding secondary ferrocenylchlorophosphine complex **83** as the major product (Scheme 2.22). The ^{31}P NMR shift as well as the extremely large P-H coupling supports complex **83** as the desired product. Still more needs to be done to further characterize and develop the chemistry of complex **83**. The implication of this reaction is that the phosphinidenoid complex may be required, or at least drastically facilitates, the insertion of the phosphinidene into the C-H bond of ferrocene.

Scheme 2.22 Generation of the chlorophosphinidene in the presence of CuCl and its subsequent insertion into the C-H bond of ferrocene

This result was one of the inspirations behind creating the extensive lists of terminal phosphinidenes organized by their method of generation, which includes the citation,

what the terminal phosphinidene was reacted with, as well as indicating if CuCl was used in the reaction (Chapter 1, Tables 1.1–1.6).

Another question we wondered was, what would be the fate of the chlorophosphinidene if it were to be generated without the presence of a substrate? After all, terminal phosphinidenes are known to oligomerize when generated without CuCl as a catalyst (Scheme 1.48 and 1.49).³⁴ Could the chlorophosphinidene oligomerize as well? When we reacted the chlorophosphole **70** with DMAD at 70°C in chloroform we were able to generate a major product **84** (with a ³¹P NMR shift of +3.1). Unfortunately preliminary attempts to purify and isolate compound **84** were unsuccessful. What we do know about this compound is that it can survive low temperature chromatography (-10°C), it elutes (together with several other products) with a 99:1 methylene chloride: acetone mixture. It does not react with 2,3-dimethyl-1,3-butadiene. And the presence of a P-Cl bond is supported by its reaction with methanol at RT to give a new compound **85** (³¹P NMR = +44.6). However, more work needs to be done to isolate and identify compound **84**.

Scheme 2.23 Generation of the chlorophosphinidene in the absence of a substrate

Lastly, it should be mentioned that recently in 2011, Mathey et. al. were trying to synthesize a 7-phosphanorbornadiene complex from a phosphole tungsten complex with a bulky substituent.³⁶ It is known that steric bulk on the phosphorus of a phosphole

can prevent the [4+2] reaction with DMAD. Despite this, they found that if they heated the bulky phosphole complex in neat DMAD they were able to successfully generate the 7-phosphanorbornadiene tungsten complex (Scheme 2.24). Normally the DMAD reacts on the phosphole face opposite to tungsten, but in their case the DMAD added on the same side as the tungsten.

Scheme 2.24 The [4+2] reaction of a bulky phosphole complex with neat dimethyl acetylenedicarboxylate

This inspired us, and we wondered if this could be the solution to finally isolate the 7-chloro-7-phosphanorbornadiene complex **72**, using neat DMAD. We reacted the chlorophosphole complex **70** with neat DMAD at 40°C for 53 hours and we were able to maximize the formation of complex **72**, and subsequently isolate it (Scheme 2.25). Its X-ray crystal structure can be seen in figure 2.7.

Scheme 2.25 The [4+2] reaction of a chlorophosphole complex **70** with neat dimethyl acetylenedicarboxylate

Figure 2.7 X-ray crystal structure of 7-chloro-7-phosphanorbornadiene tungsten complex **72**. Selected bond lengths (Å) and angles (deg): P1–W1 2.4537(12), P1–Cl1 2.0774(17), P1–C11 1.869(5), P1–C6 1.869(5), C6–C7 1.524(7), C7–C10 1.331(7), C10–C11 1.518(7), C11–C12 1.515(7), C12–C15 1.335(7), C15–C6 1.515(6); W1–P1–Cl1 109.65(6)°, C11–P1–C6 79.5(2)°, C6–P1–W1 129.30(15)°, C11–P1–W1 124.76(16)°, C6–P1–Cl1 103.84(16)°, C11–P1–Cl1 104.78(16)° Ellipsoids drawn at 30% probability level.

With its X-ray structure now known, we wanted to compare its 7-phosphanorbornadiene framework with the already published 7-phenyl-7-phosphanorbornadiene chromium complex **86**, to see if there was any insight to why complex **72** has one of the lowest documented temperatures for breaking of a 7-phosphanorbornadiene complex bridge (decomposition can already be seen occurring at 40°C in neat DMAD, another low-temperature example is the 7-cyano-7-phosphanorbornadiene tungsten complex which is known to collapse at 70°C¹⁴). Figure 2.8 compares the 7-chloro-7-phosphanorbornadiene tungsten complex **72** with the already known bond lengths and angles of the 7-phenyl-7-phosphanorbornadiene chromium complex **86**, as well as other known P–W and P–Cl bond lengths. The

bridgehead P-C bonds are slightly shorter in complex **72** compared to complex **86** [e.g. P-C4 1.869(5) vs. 1.878(3)]. This may in turn be the cause for the bridgehead angle to be slightly larger in complex **72** [**72** C1-P-C4 79.5(2)° vs. 79.0(1)° for complex **86**].

Figure 2.8 Comparing the 7-chloro-7-phosphanorbornadiene with other known bond lengths and angles

When looking at the C-C bonds in the 7-phosphanorbornadiene framework it is interesting to note that where the C=C double bonds are more similar in lengths [**72** C2-C3 1.331(7) vs. **86** C2-C3 1.337(4) and **72** C5-C6 1.335(7) vs. **86** C5-C6 1.337(4)], the C-C single bonds are all slightly shorter in complex **72** [e.g. **72** C6-C1 1.515(6) vs. **86** C6-C1 1.526(4) and **72** C4-C5 1.515(7) and **86** C4-C5 1.532(4)]. Both the P-Cl bond and the

P-W bond have increased slightly in length as expected when going from the chlorophosphole **70** to the 7-chloro-7-phosphanorborndiene **72** [**70** P-Cl 2.0546(13), **70** P-W 2.4516(8) vs. **72** P-Cl 2.0774(17), **72** P-W 2.4537(12)].

2.3 Conclusion

DFT calculations have shown the chlorophosphinidene complex **73** to be the most electrophilic phosphinidene, thus demanding further examination of its generation and reactivity. The 7-phosphanorbornadiene method appeared to be the best method for its generation, for the other known methods are difficult to transpose the synthesis for the chlorophosphinidene complexes. In order to do this, a new method was created to make the chlorophosphole complex **70**. With this new method brought higher yields as well as additional characterization (¹³C and X-ray) of the known chlorophosphole complex **70**. The chlorophosphole complex **70** has been shown to undergo [4+2] addition with activated alkenes to give the 7-chloro-7-phosphanorbornene complex **77**, or with activated alkynes to give the 7-chloro-7-phosphanorbornadiene complex **72**. Complex **72** proved to be less stable than other known 7-phosphanorbornadiene complexes and thus the generation of the chlorophosphinidene could be accomplished by a one-pot approach of heating the chlorophosphole with DMAD, as well as the substrate to trap the terminal phosphinidene. This method was used to trap the chlorophosphinidene complex **73** with alkynes, alkenes, and butadienes to give the corresponding chlorophosphirene **74**, chlorophosphirane **75**, and chlorophospholene **76** complexes, respectively. The chlorophosphirane complex **75** also proved to be another efficient precursor to the chlorophosphinidene complex. But the fact that the chlorophosphinidene complex **73** was unable to insert into the C-H bond of ferrocene without the aid of CuCl suggests that

the phosphinidenoid intermediate involved when CuCl is used, might play a bigger role in certain reactions than what was previously assumed. The 7-chloro-7-phosphanorbornadiene complex **72** was finally able to be isolated and characterized by heating the chlorophosphole complex **70** in neat DMAD at 40°C for ca. 2 days. To gain some insight into why complex **72** has one of the lowest documented temperatures for breaking of a 7-phosphanorbornadiene complex bridge, we compared its 7-phosphanorbornadiene framework with the published 7-phenyl-7-phosphanorbornadiene chromium complex **86**. From the X-ray structures it can be seen that complex **72** appears to have slightly shorter P-C bridge head lengths, a slightly larger C-P-C bridgehead angle, as well as slightly shorter C-C single bonds when compared to complex **86**. Since the differences of the 7-phosphanorbornadiene framework of complex **72** appear to be minor, the driving force for the collapse might have much more to do with the electronics of the chlorophosphinidene that is expelled. One thing is for certain, that the chlorophosphinidene is a major development in monovalent phosphorus chemistry and that its existence will play a significant role in organophosphorus chemistry.

2.4 Experimental

NMR spectra were recorded on either a 400 MHz JEOL ECA 400 or JEOL ECA 400SL spectrometer. All spectra were recorded at 298 K in CD_2Cl_2 unless otherwise specified. HRMS spectra were obtained on a Water Q-ToF Premier MS. X-Ray crystallographic analyses were performed on a Bruker X8 APEX diffractometer. All reactions were performed under argon with dried solvents. All commercially available reagents were used as received from the suppliers.

1-Chloro-3,4-dimethylphosphole pentacarbonyltungsten (**70**)

Under argon, tungsten hexacarbonyl (9.28g, 26.6mmol) was added to freshly prepared 3,4-dimethylphospholyllithium¹⁵ solution (26.6mmol) in THF (50mL), and allowed to stir overnight to form the corresponding complexed anion. Next the complexed anion solution was added dropwise to a refluxing solution (70°C) of hexachloroethane (22.00g, 92.9mmol) in THF (13mL), followed by removal of the solvent under vacuum. The crude product was then purified by flash chromatography with hexanes as the eluent ($R_F = 0.40$), solvent was then removed under vacuum, to give a yellow solid **70** (6.04g, 48.3% yield).

A slightly alternative approach involves dividing up the freshly prepared 3,4-dimethylphospholyllithium tungsten complex (26.6mmol) in THF (50mL) into 4 parts (12.5mL of solution), and adding them dropwise to 4 separate Schlenk flasks each containing hexachloroethane (22.00g, 92.9mmol) in THF (13mL) at 70°C.

Chapter 2. Generation and Trapping of a Terminal Chlorophosphinidene Complex

^{31}P NMR (CD_2Cl_2): δ 74.0 ($^1J_{\text{PW}} = 259$ Hz; $^{31}\text{P}[^1\text{H}]$ $^2J_{\text{PH}} = 41.6$ Hz); ^1H NMR (CD_2Cl_2): δ 2.17 (d, $^4J = 0.91$ Hz, $-\text{CH}_3$), 6.40 (dd, $^2J_{\text{HP}} = 41.2$ Hz, $^4J = 0.9$ Hz, $\text{H}-\text{C}=\text{C}$); ^{13}C NMR (CD_2Cl_2): δ 17.04 (d, $^3J_{\text{CP}} = 12$ Hz, $-\text{CH}_3$), 130.14 (d, $^1J_{\text{CP}} = 36$ Hz, $=\text{CH}-\text{P}$), 151.59 (d, $^2J_{\text{CP}} = 12$ Hz, $\text{Me}-\text{C}=\text{C}$), 195.48 (d, $^2J_{\text{CP}} = 8$ Hz, *cis*-CO), 198.94 (d, $^2J_{\text{CP}} = 28$ Hz, *trans*-CO).

7-Chloro-7-phosphanorborndadiene pentacarbonyltungsten (72)

1-Chloro-3,4-dimethylphosphole pentacarbonyltungsten (1.0182g, 2.16mmol) and dimethyl acetylenedicarboxylate (1.5mL, 12.2mmol) were heated in a Schlenk flask under argon for 53 hours. The crude product was then purified by column chromatography (-10°C) with a 60:40 methylene chloride: hexane mixture as the eluent, solvent was then removed under vacuum, to give a white solid (0.2898g, 22% yield). ^{31}P NMR (CD_2Cl_2) δ 189.8 ($^1J_{\text{PW}} = 269$ Hz); ^1H NMR (CD_2Cl_2) δ 2.07 (d, $J = 3.2$ Hz, 6H, CH_3), 3.82 (s, 6H, $-\text{CO}_2\text{CH}_3$), 4.00 (s, 2H, $\text{P}-\text{C}-\text{H}$); ^{13}C NMR (CD_2Cl_2) δ 16.42 (s, $-\text{CH}_3$), 53.05 (s, CO_2CH_3), 65.29 (d, $^1J_{\text{CP}} = 10.5$ Hz, $\text{P}-\text{C}-\text{H}$), 137.23 (d, $^2J_{\text{CP}} = 24.8$ Hz, $=\text{C}-\text{Me}$), 143.52 (d, $^2J_{\text{CP}} = 5.7$ Hz, $=\text{C}-\text{CO}_2\text{Me}$), 164.91 (d, $^3J_{\text{CP}} = 3.8$ Hz, $-\text{CO}_2\text{Me}$), 195.38 (d, $^2J_{\text{CP}} = 6.7$ Hz, *cis*-CO), 197.36 (d, $^2J_{\text{CP}} = 37.2$ Hz, *trans*-CO). HRMS m/z 611.9562 (calcd for $\text{C}_{17}\text{H}_{14}\text{O}_9\text{ClP}^{184}\text{W}$, 611.9574).

1-Chlorophosphirane pentacarbonyltungsten (75)

An excess of dimethyl acetylendicarboxylate (2.5mL, 20.3 mmol) and cyclohexene (12mL, 118mmol) were added to a Schlenk flask containing 1-chloro-3,4-dimethylphosphole pentacarbonyltungsten (1.00g, 2.1 mmol) in toluene (5mL). The reaction mixture was then heated under argon, at 75°C for 18 hours. Solvent was then removed under vacuum. Next the product was purified by chromatography (0°C) on silica gel with hexanes as the eluent ($R_F = 0.55$), solvent was then removed under vacuum, to give a white solid (0.390g, 38.9% yield).

^{31}P NMR (CD_2Cl_2): δ -64.0 ($^1J_{\text{PW}} = 298$ Hz); ^{13}C NMR (CD_2Cl_2): δ 21.64 (d, $J_{\text{CP}} = 3.6$ Hz, CH_2), 22.23 (d, $J_{\text{CP}} = 2.4$ Hz, CH_2), 28.49 (d, $^1J_{\text{CP}} = 21.9$ Hz, CH-P), 195.45 (d, $J_{\text{CP}} = 8.5$ Hz, *cis*-CO), 198.05 (d, $J_{\text{CP}} = 41.3$ Hz, *trans*-CO).

1-Chloro-3,4-dimethylphosphol-3-ene pentacarbonyltungsten (76)

An excess of 2,3-dimethyl-1,3-butadiene and dimethyl acetylendicarboxylate were added to a Schlenk flask containing 1-chloro-3,4-dimethylphosphole pentacarbonyltungsten (84.0mg, 0.18mmol) in toluene (2.5mL). The reaction mixture was then heated under argon, at 70°C for 16 hours. Solvent was then removed under vacuum. Next the reaction flask was cooled to -10°C and a minimal amount of pentane was used to extract the product from the byproducts. Next the product was purified by

chromatography (0°C) on silica gel with methylene chloride as the eluent ($R_F = 0.63$), solvent was then removed under vacuum, to give a white solid (15mg, 18% yield).

^{31}P NMR (toluene): δ 116.0 ($^1J_{\text{PW}} = 264$ Hz); ^1H NMR (CD_2Cl_2): δ 1.77 (s, CH_3), 2.90 (ABX, $\text{CH}_2\text{-P}$); ^{13}C NMR (CD_2Cl_2): δ 16.33 (d, $^3J_{\text{CP}} = 7.4$ Hz, CH_3), 50.75 (d, $^1J_{\text{CP}} = 24.6$ Hz, $\text{CH}_2\text{-P}$), 129.67 (s, Me-C=), 196.74 (d, $^2J_{\text{CP}} = 7.4$ Hz, *cis*-CO), 200.34 (d, $^2J_{\text{CP}} = 23.4$ Hz, *trans*-CO).

7-Chloro-7-phosphanorbornene pentacarbonyltungsten (77)

1-Chloro-3,4-dimethylphosphole (200mg, 0.425mmol) and *N*-phenylmaleimide (1.2 eq., 88.3 mg, 0.51mmol) were dissolved in dry toluene (2 mL). The reaction mixture was heated at 60°C under argon for 5.5 hours giving the 7-chloro-7-phosphanorbornene. Solvent was removed under vacuum. Product was purified on silica gel with a dichloromethane:hexane 40:60 mixture as the eluent ($R_F = 0.13$), solvent was then removed under vacuum, to give a white solid (0.195g, 71.3% yield).

^{31}P NMR (CD_2Cl_2): δ 86.2 ($^1J_{\text{PW}} = 278.8$ Hz); ^1H NMR (CD_2Cl_2): δ 1.92 (d, $J = 2.8$ Hz, 6H, CH_3), 3.59 (s, 2H C-H), 4.10 (s, 2H, C-H), 7.10 (d, $^3J_{\text{HH}} = 7.4$ Hz, 2H, Ph-H), 7.42 (m, 3H, Ph-H); HRMS: $m/z = 642.9745$ (calcd for $\text{C}_{21}\text{H}_{15}\text{NO}_7\text{P}^{37}\text{Cl}^{182}\text{W}$, 642.9727).

7-Fluoro-7-phosphanorbornene pentacarbonyltungsten (78)

Tetra-butylammonium fluoride (0.16mL, 0.160mmol) was added dropwise to a Schlenk containing 7-chloro-7-phosphanorbornene complex (100mg, 0.155mmol) in dry THF (2mL) under argon at room temperature. The reaction was stirred for 10 minutes. Solvent was removed under vacuum and the crude mixture was purified by column chromatography (0°C) with a 50:50 hexane: dichloromethane mixture as the eluent (R_F = 0.18), solvent was then removed under vacuum, to give a white solid (36.9mg, 37.9% yield).

^{31}P NMR (CH_2Cl_2): δ 150.4 ($^1J_{\text{PW}} = 288.6$ Hz, $^1J_{\text{PF}} = 943.9$ Hz); ^{19}F NMR (CH_2Cl_2): δ -88.0 ($^1J_{\text{FP}} = 941.7$ Hz); ^1H NMR (CD_2Cl_2): δ 1.88 (pseudo-t, $J = 1.8$ Hz, 6H, CH_3), 3.53 (pseudo-hextet, $J = 1.8$ Hz, 2H, C-H), 3.87 (pseudo-q, $J = 1.8$ Hz, 2H, C-H), 7.08 (m, 2H, *o*-H), 7.47 (m, 3 H, *p* and *m*-H); HRMS: $m/z = 626.0079$. (calcd for $\text{C}_{21}\text{H}_{15}\text{NO}_7\text{FP}^{183}\text{W}$, 626.0073).

1-Chloro-2-trimethylsilylphosphirene pentacarbonyltungsten (81) **Method A:** One-pot approach

1-Chloro-3,4-dimethylphosphole complex (1) (0.4990g, 1.06mmol) was dissolved in dry toluene (10mL) in a Schlenk under argon, after which dimethylacetylene dicarboxylate (2.5ml, 20.3mmol) and trimethylsilylacetylene (2.5ml, 17.7mmol) were added. The reacting mixture was heated at 70°C for 24h. Solvent was removed under vacuum, and

the thick viscous crude product was purified by column chromatography on silica gel using hexanes as the eluent ($R_F = 0.45$), solvent was then removed under vacuum, to give a white solid (92.6mg, 17.9% yield).

Method B: 1-Chlorophosphirane approach

1-Chlorophosphirane pentacarbonyltungsten complex (0.234g, 0.495mmol) and trimethylsilylacetylene (1.4mL, 9.91mmol) were dissolved in dry toluene (1.8mL) in a Schlenk, under argon. The reaction was heated for 2.5h at 75°C. The solvent was removed under vacuum and the crude product was purified on silica gel using hexanes as the eluent ($R_F = 0.40$), solvent was then removed under vacuum, to give a white solid (0.131g, 54.3% yield).

^{31}P NMR (CD_2Cl_2) δ -119.6 ($^1J_{\text{PW}} = 331$ Hz, $^{31}\text{P}[\text{H}]$ $^2J_{\text{PH}} = 22.3$ Hz); ^1H NMR (CD_2Cl_2) δ 0.41 (s, 9H, -SiMe₃) 9.52 (d, $^2J_{\text{HP}} = 22.0$ Hz, 1H, C-H); ^{13}C NMR (CD_2Cl_2) δ -1.67 (s, SiMe₃) 153.7 (d, $^1J_{\text{CP}} = 28.8$ Hz, =C-H) 161.8 (d, $^1J_{\text{CP}} = 49.8$ Hz, =C-SiMe₃) 195.8 (d, $^2J_{\text{CP}} = 8.6$ Hz, *cis*-CO) 198.9 (d, $^2J_{\text{CP}} = 50.8$ Hz, *trans*-CO). HRMS m/z 487.9241 (calcd for C₁₀H₁₀ClO₅PSi¹⁸⁴W, 487.9233).

1-Chloro-2-phenyl-3-phosphirene pentacarbonyltungsten (82a,b)

1-Chlorophosphirane pentacarbonyltungsten complex (0.302g, 0.639mmol), styrene (1.5mL, 13.1mmol), and dry toluene (2mL) were added to a Schlenk under argon. The reaction mixture was then heated at 75°C for 3h. Solvent was subsequently removed under vacuum and the crude product was purified by column chromatography (0°C) on silica gel with hexanes as the eluent, solvent was then removed under vacuum, to give

two isomers: **82a**, a light yellow oil, $R_F = 0.40$ and **82b** a light yellow crystalline solid, $R_F = 0.33$, (**82a,b**, 0.316g, 88.7% yield).

82a ^{31}P NMR (CD_2Cl_2) δ -76.42 ($^1J_{\text{PW}} = 308.2$ Hz); ^1H NMR (CD_2Cl_2) δ 2.04 (q, $J = 10.0$ Hz, 1H), 2.51 (m, 1H), 3.61 (q, $J = 10.0$ Hz, 1H), 7.25 (m, 2H, *ortho*-H), 7.35 (m, 3H, *meta/para*-H); ^{13}C NMR (CD_2Cl_2) δ 20.92 (d, $^1J_{\text{CP}} = 21.9$ Hz), 33.88 (d, $^1J_{\text{CP}} = 23.8$ Hz, C-H), 128.37 (d, $^5J_{\text{CP}} = 3.8$ Hz, *para*-CH), 128.75 (d, $^4J_{\text{CP}} = 5.7$ Hz, *meta*-CH), 129.53 (d, $^3J_{\text{CP}} = 2.9$ Hz, *ortho*-CH), 135.37 (s, *ipso*-C), 194.53 (d, $^2J_{\text{CP}} = 8.6$ Hz, *cis*-CO), 197.71 (d, $^2J_{\text{CP}} = 45.8$ Hz, *trans*-CO). HRMS m/z 493.9291 (calcd for $\text{C}_{13}\text{H}_8\text{O}_5\text{ClP}^{184}\text{W}$, 493.9307).

82b ^{31}P NMR (CD_2Cl_2) δ -76.05 ($^1J_{\text{PW}} = 303.2$ Hz); ^1H NMR (CD_2Cl_2) δ 1.98 (m, 1H), 2.40 (dt, $^1J = 7.70$ Hz, $^2J = 10.42$ Hz, 1H), 3.03 (dt, $^1J = 11.3$ Hz, $^2J = 10.9$ Hz, 1H), 7.39 (m, 5H, Ph-H); ^{13}C NMR (CD_2Cl_2) δ 19.23 (d, $^1J_{\text{CP}} = 20.0$ Hz, CHPh), 32.57 (d, $^1J_{\text{CP}} = 23.8$ Hz, CH_2), 127.57 (d, $^5J_{\text{CP}} = 1.9$ Hz, *para*-CH), 128.58 (s, *meta*-CH), 128.88 (d, $^3J_{\text{CP}} = 3.9$ Hz, *ortho*-CH), 133.36 (d, $^2J_{\text{CP}} = 6.6$ Hz, *ipso*-C), 194.59 (d, $^2J_{\text{CP}} = 8.6$ Hz, *cis*-CO), 197.71 (d, $^2J_{\text{CP}} = 44.8$ Hz, *trans*-CO). HRMS m/z 493.9291 (calcd for $\text{C}_{13}\text{H}_8\text{O}_5\text{ClP}^{184}\text{W}$, 493.9307).

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CHAPTER 3

Synthesis and Chemistry of 2-Phosphafurans

3.1 Introduction

Of the extensive family of heterophospholes, 2-phosphafurans (or 1,2-oxaphospholes) are among the simplest and yet least well known.¹ In fact, only one compound of this class has ever been described in the literature. In 1999, Regitz et. al. were the first to generate the 2-phosphafuran via a complex route (Scheme 3.1).² The reaction first begins with the synthesis of mesitylphosphaalkene **87**. The mesitylphosphaalkene **87** is then subjected to high-temperature vacuum thermolysis to generate the 1,2,4-oxadiphosphole **88**. After a sequence of bulb-to-bulb distillations and recrystallizations the 1,2,4-oxadiphosphole **88** can be isolated in low yield. As they were testing the reactivity of the new 1,2,4-oxadiphosphole **88**, they found that when it was reacted with dimethyl acetylenedicarboxylate at low temperature it generated the 2-phosphafuran **89** and mesitylphosphaacetylene concomitantly. Due to its instability, Regitz et. al. only managed to characterize the 2-phosphafuran **89** by ³¹P NMR at low temperature.

Scheme 3.1 Synthesis of the first 2-phosphafuran

Schleyer et al. have computed 2-phosphafurans to be reasonably aromatic with an ASE (aromatic stabilization energy) of 13.19 kcal mol⁻¹, and a NICS(1) (nucleus-independent chemical shift) value of -9.34 ppm.³ Systems with strongly positive ASEs are aromatic, while those with strongly negative ones are antiaromatic. For NICS calculations the more negative the NICS value, the more aromatic it is. Conversely, the more positive the NICS value the more antiaromatic the system is. Figure 3.1 gives the aromaticity calculation values of 2-phosphafuran as compared to other heterocycles.³

ASE (in kcal/mol)	13.19	3.20	14.77	18.57	20.57
NICS(1) (in ppm)	-9.34	-5.97	-9.36	-10.79	-10.60

Figure 3.1 Aromaticity based calculation of 2-phosphafuran compared with other heterocycles

We wish to report here the straightforward synthesis of a 2-phosphafuran as a reasonably stable species and to give some preliminary results concerning its chemistry.

3.2 Results and discussion

Our approach takes full advantage of the availability of the transient chlorophosphinidene complex **73** (Scheme 3.2).⁴

Scheme 3.2 Generation of the chlorophosphinidene complex

Using the one-pot approach, to trap the chlorophosphinidene complex **73** as soon as it is generated, we heated the chlorophosphole complex **70**, dimethyl acetylenedicarboxylate (DMAD) and benzylideneacetophenone at 80°C for 8 hours to obtain the [1+4] cycloadduct, the chlorophosphinite complex **90**, as a mixture of two isomers (Scheme 3.3).

Scheme 3.3 One-pot reaction to generate chlorophosphinidene complex and subsequently trap it with benzylideneacetophenone

Next the cycloadduct **90** was reacted with *N*-methylimidazole at -20°C to give a red solution of the very reactive 2-phosphafuran complex **91** (Scheme 3.4).

Scheme 3.4 Generation of the first complexed 2-phosphafuran

This species was characterized by its low field ^{31}P resonance δ (^{31}P) 222.6 ($^1J_{\text{PW}} = 293$ Hz). It can be kept without noticeable decomposition (i.e. a drastic decrease in signal-to-noise ratio) at room temperature for 1 hour and for 2 weeks at -25°C. Attempts to purify the 2-phosphafuran complex **91** by chromatography at (-10°C) were unsuccessful. To definitively establish its identity we performed a series of trapping reactions. The 2-phosphafuran complex **91** reacts with 2,3-dimethyl-1,3-butadiene to give the bicyclic phosphinite complex **92** (Scheme 3.5). The X-ray crystal structure of complex **92** can be seen in figure 3.2. In this reaction the butadiene reacts with the P=C double bond of the 2-phosphafuran complex.

Scheme 3.5 Reaction of 2-phosphafuran complex **91** with 2,3-dimethyl-1,3-butadiene

Figure 3.2 X-ray crystal structure of the bicyclic tungsten complex **92**. Selected bond lengths (Å) and angles (deg): P1–W1 2.4674(5), P1–C12 1.883(2), P1–C6 1.826(2), P1–O6 1.6608(15), O6–C20 1.399(2), C20–C19 1.331(3), C19–C12 1.513(3), C12–C11 1.568(3), C11–C9 1.519(3), C9–C7 1.346(3), C7–C6 1.512(3); W1–P1–C12 127.92(6)°, W1–P1–O6 113.13(5)°, W1–P1–C6 115.50(7)°, O6–P1–C6 103.14(9)°, O6–P1–C12 94.94(8)°, C6–P1–C12 98.06(9)°. Ellipsoids drawn at 50% probability level.

We then tested the reaction of the 2-phosphafuran complex **91** with an activated alkene. 2-Phosphafuran complex **91** reacts with *N*-phenylmaleimide at low temperature to give the tricyclic phosphinite complex **93** (Scheme 3.6). The X-ray crystal structure of complex **93** can be seen in figure 3.3. In this reaction, it is the phosphadienic system of the 2-phosphafuran that is reacting with *N*-phenylmaleimide.

Scheme 3.6 Reaction of 2-phosphafuran complex **91** with *N*-phenylmaleimide

Figure 3.3 X-ray crystal structure of the bicyclic tungsten complex **93**. Selected bond lengths (Å) and angles (deg): P1–W1 2.4171(7), P1–O6 1.6475(19), P1–C6 1.842(3), P1–C10 1.882(3), C6–C7 1.338(4), C7–C8 1.508(4), C8–C9 1.587(4), C9–C10 1.534(4); W1–P1–O6 116.22(7), W1–P1–C6 128.50(9), W1–P1–C10 124.45(9), P1–O6–C8 102.56(15). Ellipsoids drawn at 50% probability level.

Finally, 2-Phosphafuran complex **91** was reacted with methanol to give two corresponding isomers of the cyclic phosphonite complex **94**. In this reaction methanol is added across the P=C double bond of the phosphafuran.

Scheme 3.7 Reaction of 2-phosphafuran complex **91** with methanol

The fact that 2-phosphafurans are computed to be reasonable aromatic (ASE 13.19 kcal mol⁻¹)³ explains why it is possible to synthesize these species by dehydrochlorination of

complex **90** with a mild base (Scheme 3.4). Unfortunately, this aromaticity is not high enough to suppress the reactivity of the P=C double bond. Indeed, it is surprising to see that the 2-phosphafuran complex **91** reacts similar to that of nonaromatic 2H-phospholes.⁵ Of course all of these reactions have concerned the complexed 2-phosphafuran and it must be recalled that phosphorus complexation is known to reduce the aromaticity of related species such as phosphinines.⁶ Thus, what is the reactivity of the free species?

We discovered that if we heat the 2-phosphafuran complex **91** in the presence of an excess of *N*-methylimidazole for 2 hours at 60°C we obtain the free 2-phosphafuran **95** (Scheme 3.8). The free 2-phosphafuran displays a ³¹P resonance at 285.5 ppm in toluene with no P–W coupling. This reaction suggests that the 2-phosphafuran is a poor P-donor.

Scheme 3.8 Decomplexation of 2-phosphafuran tungsten complex with *N*-methylimidazole to generate the free 2-phosphafuran

The phosphafuran **95** can be kept at room temperature for 10 days without noticeable decomposition. Attempts to purify the phosphafuran **95** by column chromatography at (-10°C) were unsuccessful. To absolutely confirm its identity we decided to perform a trapping experiment. We reacted the free phosphafuran **95** with 2,3-dimethyl-1,3-butadiene followed by sulfurization to give the bicyclic phosphinite sulfide **97** (Scheme

3.9). The bicyclic phosphinite sulfide **97** was completely characterized. Its X-ray structure can be seen in figure 3.4.

Scheme 3.9 Reaction of the free 2-phosphafuran with 2,3-dimethyl-1,3-butadiene followed by sulfurization

Figure 3.4 X-ray crystal structure of the bicyclic phosphorus sulfide **97**. Selected bond lengths (Å) and angles (deg): P1–S1 1.9263(4), P1–O1 1.6353(8), P1–C3 1.8673(11), P1–C7 1.8071(12), C7–C6 1.5164(17), C6–C5 1.3423(17), C5–C4 1.5183(16), C4–C3 1.5602(16), C3–C2 1.5122(15), C2–C1 1.3351(16), C1–O1 1.4049(13); S1–P1–C7 115.72(4), S1–P1–O1 113.31(4), S1–P1–C3 119.88(4), O1–P1–C3 96.23(4), O1–P1–C7 103.73(5). Ellipsoids drawn at 50% probability level.

Clearly, the complexation by tungsten provides some kinetic stability to the 2-phosphafuran ring by steric protection as it does for 2*H*-phospholes⁷ but does not fundamentally alter the reactivity of the ring.

The preceding work was published in 2010 in Organometallics.⁸ The following section includes unpublished results as well as some preliminary experiments.

Since the 2-phosphafuran tungsten complex **91** results in noticeable decomposition at room temperature after 1 hour, we wondered if we could further stabilize the system by complexing the reactive P=C double bond. Previously Mathey et al. have shown pentacarbonyltungsten as an effective η^2 -complexing group for the P=C double bond.^{9,10} Unfortunately our attempts to complex the P=C double bond with tungsten were unsuccessful (Scheme 3.10).

Scheme 3.10 Unsuccessful attempts to π -complex the reactive P=C double bond of the 2-phosphafuran complex with pentacarbonyltungsten

We were also curious to see if we could π -complex the 2-phosphafuran as an η^5 -complex of a transition metal. After all, η^5 -complexes of furans are extremely rare.¹¹ To our knowledge only one example has ever been reported in the literature, which was described as being unstable and only observed in solution.¹² We wondered if having the phosphorus incorporated into the furan ring would allow it to be a better π -ligand than merely furan. Unfortunately, our preliminary attempts to π -complex the 2-phosphafuran to chromium tricarbonyl were unsuccessful (Scheme 3.11).

Scheme 3.11 Unsuccessful attempt to π -complex the free 2-phosphafuran with chromiumtricarbonyl

Although the preliminary attempts to π -complex the 2-phosphafuran failed, we believe further tests need to be done. For example, one reason that the π -complex of the 2-phosphafuran could have failed could be due to trace amounts of *N*-methylimidazole in the solution (used for decomplexation of the tungsten), which could compete as a ligand for the transition metal centers.

3.3 Conclusion

2-Phosphafurans are one of the least well-known members of the heterophosphole family. One reason for this lies in the fact that there lacks a straightforward method to their synthesis. Only one compound of this class has been described in the literature as an unstable species, generated via a complex route. Recently we have described the generation and trapping of a chlorophosphinidene complex $[(\text{CO})_5\text{W} \leftarrow \text{P}-\text{Cl}]$. In this report, we demonstrate the potential of this terminal phosphinidene by utilizing it to synthesize the unfamiliar 2-phosphafuran. Trapping the chlorophosphinidene with benzylideneacetophenone, followed by a dehydrochlorination with a mild base, the 2-phosphafuran tungsten complex was able

to be generated. This complex is moderately stable, yet reactive, as can be seen by its reactions with alkynes, butadienes, and methanol at low temperature. In the presence of excess *N*-methylimidazole the tungsten complexed 2-phosphafuran can be decomplexed to give the free 2-phosphafuran, which also demonstrates that the 2-phosphafuran is a poor P-donor. Calculations predict the 2-phosphafuran to be reasonably aromatic. Unfortunately the aromaticity of the 2-phosphafuran is not high enough to suppress the reactivity of the P=C double bond, as can be seen by its reaction with 2,3-dimethyl-1,3-butadiene. From its reactions, we can see that 2-phosphafurans behave similarly to nonaromatic 2*H*-phospholes. Although preliminary attempts to further complex the P=C double bond of the 2-phosphafuran tungsten complex or to η^5 -complex the free 2-phosphafuran were unsuccessful, further investigation should be pursued.

With this new straightforward synthesis of 2-phosphafurans we have already begun to learn some preliminary results concerning 2-phosphafurans and their complexes as well as their chemistry. As we gain more insight into these species we can begin to think about their utilization for complexes and as building blocks for making new organophosphorus compounds.

3.4 Experimental

Toluene was dried before use. Silica gel (230-400 mesh) was used for the chromatographic separations. NMR spectra were recorded on either a JEOL ECA 400, or JEOL ECA 400SL spectrometer. All spectra were recorded at 298K in CD₂Cl₂ unless otherwise specified. HRMS spectra were obtained on a Water Q-ToF Premier MS. X-ray crystallographic analyses were performed on a Bruker X8 APEX diffractometer. All reactions were performed under argon. All commercially available reagents were used as received from the suppliers.

[1+4] Cycloadduct, Chlorophosphinite pentacarbonyltungsten (**90a,b**)

1-chloro-3,4-dimethylphosphole complex (1.49g, 3.2mmol), excess dimethyl acetylenedicarboxylate, and benzylideneacetophenone (1.65, 7.9mmol) are heated at 80°C, under argon, in toluene (20mL). The reaction is monitored by ³¹P NMR and takes about 8-9hrs. The solvent is then evaporated and the product is purified on silica gel (at 0°C) using a 90:10 hexane:dichloromethane mixture as the eluent (*R_F* = 0.33), solvent was then removed under vacuum, to give a transparent-light grey sticky wax (1.10g, 57.9% yield). The product is a mixture of 2 isomers in approximately a 70:30 ratio.

Data for **90a** are as follows: ³¹P NMR (CD₂Cl₂): δ 178.4, ¹*J*_{PW} = 341 Hz; ¹H NMR (CD₂Cl₂): δ 5.32 (dd, *J*_{HH} = 1.3 Hz, *J*_{HP} = 26.2 Hz, 1H, P-C-H), 6.18 (dd, *J*_{HH} = 2.3 Hz, *J*_{HP} = 18.1 Hz, 1H, =CH), 7.37 (m, Ph), 7.51-7.64 (m, Ph) 7.87-7.92 (m, Ph); ¹³C NMR (CD₂Cl₂): δ 66.36 (d, *J*_{CP} = 5.7 Hz, P-C-H), 104.98 (s, =CH), 158.35 (d, *J*_{CP} = 8.6 Hz, Ph-C-O), 195.11 (d, *J*_{CP} = 8.6 Hz, *cis* CO), 198.20 (d, *J*_{CP} = 42.0 Hz, *trans* CO).

Data for **90b** are as follows: ^{31}P NMR (CD_2Cl_2): δ 182.6, $^1J_{\text{PW}} = 346$ Hz; ^1H NMR (CD_2Cl_2): δ 4.88 (dd, $J_{\text{HH}} = 3.7$ Hz, $J_{\text{HP}} = 6.8$ Hz, 1H, P-C-H), 6.27 (dd, $J_{\text{HH}} = 3.6$ Hz, $J_{\text{HP}} = 19.9$ Hz, 1H, =CH), 7.37 (m, Ph), 7.51-7.64 (m, Ph) 7.87-7.92 (m, Ph); ^{13}C NMR (CD_2Cl_2): δ 67.65 (d, $J_{\text{CP}} = 4.7$ Hz, P-C-H), 105.59 (s, =CH), 158.08 (d, $J_{\text{CP}} = 8.6$ Hz, Ph-C-O), 194.55 (d, $J_{\text{CP}} = 8.5$ Hz, *cis* CO), 198.11 (d, $J_{\text{CP}} = 42.9$ Hz, *trans* CO).

HRMS m/z 597.9589 (calcd for $\text{C}_{20}\text{H}_{12}\text{ClO}_6\text{P}^{184}\text{W}$, 597.9570).

Bicyclic phosphinite pentacarbonyltungsten (**92**)

The [1+4] cycloadduct (0.126g, 0.21mmol) is first dissolved in toluene (2.5mL) and added to a Schlenk under argon. At -20°C 1-methylimidazole (0.1mL, 1.2mmol) is added dropwise to the cycloadduct, and is allowed to stir for 10 min, the solution turns yellowish-orange. The solution is then allowed to warm up to room temperature slowly, and the color changes to an orange-red solution. ^{31}P NMR confirms the complexed phosphafuran is generated. The solution is then lowered again to -20°C and 2,3-dimethyl-1,3-butadiene (0.1mL, 0.88mmol) is added dropwise, and is allowed to stir for 10 min. Solution is allowed to warm up to room temperature slowly and then checked by ^{31}P NMR. Once the trapping reagent is added the solution changes to light yellow. Solvent was removed under vacuum and the product is purified on silica gel (at 0°C) using a 90:10 hexane:dichloromethane mixture as the eluent ($R_f = 0.38$), solvent was then removed under vacuum, to give a white-light yellow solid (0.132g, 97% yield). ^{31}P NMR (CD_2Cl_2): δ 159.6, $^1J_{\text{PW}} = 281$ Hz; ^1H NMR (CD_2Cl_2): δ 1.82 (broad s, 3H, CH_3), 1.86 (s, 3H, CH_3), 2.66 (m, 1H, CH_2), 3.00 (m, 2H, CH_2), 3.28 (m, 1H, CH_2), 5.63 (d, $J_{\text{HP}} =$

17.9 Hz, =CH) 7.31-7.45 (m, 8H, Ph), 7.67 (m, 2H, Ph); ^{13}C NMR (CD_2Cl_2): δ 20.86 (d, $J_{\text{CP}} = 2.5$ Hz, CH_3), 21.19 (d, $J_{\text{CP}} = 2.5$ Hz, CH_3), 43.37 (s, CH_2), 45.12 (d, $J_{\text{CP}} = 9.8$ Hz, CH_2), 61.09 (d, $J_{\text{CP}} = 17.1$ Hz, P-C-Ph), 106.56 (d, $J_{\text{CP}} = 3.7$ Hz, =CH), 157.36 (d, $J_{\text{CP}} = 6.1$ Hz, =C(Ph)O), 195.95 (d, $J_{\text{CP}} = 7.4$ Hz, *cis* CO), 199.75 (d, $J_{\text{CP}} = 29.5$ Hz, *trans* CO).
 HRMS m/z 644.0591 (calcd for $\text{C}_{26}\text{H}_{21}\text{O}_6\text{P}^{184}\text{W}$, 644.0585).

Tetracyclic phosphinite pentacarbonyltungsten (93)

The [1+4] cycloadduct (0.217g, 0.36mmol) is first dissolved in toluene (2.5mL) and added to a Schlenk under argon. At -20°C 1-methylimidazole (0.1mL, 1.2mmol) is added dropwise to the cycloadduct, and is allowed to stir for 10 min, the solution turns yellowish-orange. The solution is then allowed to warm up to room temperature slowly, and the color changes to an orange-red solution. ^{31}P NMR confirms the complexed phosphafuran is generated. The solution is then lowered again to -20°C and *N*-phenylmaleimide (0.085g, 0.49mmol) is added, and is allowed to stir for 10 min. Solution is allowed to warm up to room temperature slowly and then checked by ^{31}P NMR. Once the trapping reagent is added the solution changes to light yellow. Solvent was removed under vacuum and the product is purified on silica gel (at 0°C) using dichloromethane as the eluent, solvent was then removed under vacuum, to give a light yellow solid (0.262g, 98% yield).

^{31}P NMR (CD_2Cl_2): δ 117.8, $^1J_{\text{PW}} = 308$ Hz; ^1H NMR (CD_2Cl_2): δ 4.05 (dd, $J_{\text{HH}} = 7.7$ Hz, $J_{\text{HP}} = 2.7$ Hz, 1H, CH-CO), 4.38 (dd, $J_{\text{HH}} = 7.7$ Hz, $J_{\text{HP}} = 3.2$ Hz, 1H, CH-CO), 6.80 (m, 2H, Ph), 7.27-7.59 (m, 11H, Ph), 7.93 (m, 2H, Ph); ^{13}C NMR (CD_2Cl_2): δ 51.93 (s, CH(CO)), 53.84

(d, $J_{CP} = 7.3$ Hz, P-CH(CO)), 98.23 (d, $J_{CP} = 3.7$ Hz, (Ph)-C-O), 142.68 (s, =CH), 171.51 (s, NCO), 172.97 (s, NCO), 194.35 (d, $J_{CP} = 8.5$ Hz, *cis* CO), 197.29 (d, $J_{CP} = 34.1$ Hz, *trans* CO). HRMS m/z 735.0273 (calcd for $C_{30}H_{18}NO_8P^{184}W$, 735.0280).

Phosphonite pentacarbonyltungsten (**94a,b**)

The [1+4] cycloadduct (0.374g, 0.62mmol) is first dissolved in toluene (4mL) and added to a Schlenk under argon. At -20°C 1-methylimidazole (0.1mL, 1.2mmol) is added dropwise to the cycloadduct, and is allowed to stir for 10 min, the solution turns yellowish-orange. The solution is then allowed to warm up to room temperature slowly, and the color changes to an orange-red solution. ^{31}P NMR confirms the complexed phosphafuran is generated. The solution is then lowered again to -20°C and methanol (0.2mL, 4.9mmol) is added dropwise, and allowed to stir for 10 min. Solution is allowed to warm up to room temperature slowly and then checked by ^{31}P NMR. Once the trapping reagent is added the solution changes to light yellow. Solvent was removed under vacuum and the product is purified on silica gel (at 0°C) using a 90:10 pentane:dichloromethane mixture as the eluent, solvent was then removed under vacuum, to give 2 isomers. Isomer **94a** is a clear light-yellow thick oil (0.117g) and Isomer **94b** is a light yellow solid (0.161g). Total for the 2 isomers (0.278g, 74.9% yield).

Data for **94a** are as follows: ^{31}P NMR (CD_2Cl_2): δ 171.9, $^1J_{PW} = 331$ Hz; 1H NMR (CD_2Cl_2): δ 3.42 (d, $J_{HP} = 12.4$ Hz, 3H, OCH_3), 4.86 (dd, $J_{HH} = 2.3$ Hz, $J_{HP} = 14.6$ Hz, 1H, P-C-H), 6.01 (dd, $J_{HH} = 2.3$ Hz, $J_{HP} = 18.3$ Hz, 1H, =CH), 7.34-7.49 (m, 8H, Ph), 7.78 (m, 2H, Ph); ^{13}C NMR (CD_2Cl_2): δ 55.45 (d, $J_{CP} = 3.9$ Hz, OCH_3), 62.91 (d, $J_{CP} = 18.2$ Hz, P-C-H), 103.61

(s, =CH), 157.08 (d, J_{CP} = 6.7 Hz, Ph-C-O), 195.82 (d, J_{CP} = 8.7 Hz, *cis* CO), 198.55 (d, J_{CP} = 34.6 Hz, *trans* CO).

HRMS m/z 594.0076 (calcd for $C_{21}H_{15}O_7P^{184}W$, 594.0065).

Data for **94b** are as follows: ^{31}P NMR (CD_2Cl_2): δ 185.6, $^1J_{PW}$ = 336 Hz; 1H NMR (CD_2Cl_2):

δ 3.75 (d, J_{HP} = 11.4 Hz, 3H, OCH_3), 4.45 (dd, J_{HH} = 3.7 Hz, J_{HP} = 9.6 Hz, 1H, P-C-H),

6.04 (dd, J_{HH} = 3.7 Hz, J_{HP} = 19.3 Hz, 1H, =CH), 7.25-7.52 (m, 8H, Ph), 7.82 (m, 2H, Ph);

^{13}C NMR (CD_2Cl_2): δ 55.20 (d, J_{CP} = 8.7 Hz, OCH_3), 59.68 (d, J_{CP} = 13.5 Hz, P-C-H), 103.99

(s, =CH), 157.80 (d, J_{CP} = 6.7 Hz, Ph-C-O), 195.32 (d, J_{CP} = 9.6 Hz, *cis* CO), 198.68 (d, J_{CP} =

35.5 Hz, *trans* CO).

HRMS m/z 594.0063 (calcd for $C_{21}H_{15}O_7P^{184}W$, 594.0065).

Bicyclic phosphinite sulfide complex (97)

The [1+4] cycloadduct (0.394g, 0.66mmol) is first dissolved in toluene (4mL) and added to a Schlenk under argon. At -20°C 1-methylimidazole (0.1mL, 1.2mmol) is added dropwise to the cycloadduct, and is allowed to stir for 10 min, the solution turns yellowish-orange. The solution is then allowed to warm up to room temperature slowly, and the color changes to an orange-red solution. ^{31}P NMR confirms the complexed phosphafuran is generated. Next the reaction is heated at 60°C for 2 hours to obtain the free 2-Phosphafuran. Next at room temp. 2,3-dimethyl-1,3-butadiene (1.0mL, 8.8mmol) is added to the solution. The solution is then allowed to stir overnight, and checked by ^{31}P NMR. Next sulfur (0.210g, 0.66mmol) is added at room temp, and the mixture is allowed to stir for 1 hour. Solvent was removed under vacuum and the product is

purified on silica gel using a 60:40 hexane:dichloromethane mixture as the eluent, solvent was then removed under vacuum, to give a white solid (0.133g, 57.3% yield).

^{31}P NMR (CD_2Cl_2): δ 123.5 ; ^1H NMR (CD_2Cl_2): δ 1.74 (d, $J_{\text{HP}} = 5.0$ Hz, 3H, CH_3), 1.79 (s, 3H, CH_3), 2.61 (m, 1H, CH_2), 3.09 (m, 2H, CH_2), 3.35 (m, 1H, CH_2), 5.64 (d, $J_{\text{HP}} = 24.7$ Hz, =CH), 7.29-7.44 (m, 8H, Ph), 7.62 (m, 2H, Ph); ^{13}C NMR (CD_2Cl_2): δ 20.67 (d, $J_{\text{CP}} = 6.7$ Hz, CH_3), 21.29 (d, $J_{\text{CP}} = 2.9$ Hz, CH_3), 41.66 (d, $J_{\text{CP}} = 56.6$ Hz, CH_2), 42.53 (s, CH_2), 55.01 (d, $J_{\text{CP}} = 59.4$ Hz, P-C-Ph), 107.89 (d, $J_{\text{CP}} = 5.8$ Hz, =CH), 156.97 (s, =C(Ph)O).

HRMS m/z 375.0960 (calcd for $\text{C}_{21}\text{H}_{21}\text{NaOPS}$, 375.0948).

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CHAPTER 4

Hydroxyphosphinidenes as a Source of New Phosphinous Acids

4.1 Introduction

Classical trivalent phosphinous acids **98** are unstable and readily rearrange by prototropy to their pentavalent secondary phosphine oxide **99** counterpart (Scheme 4.1).

Scheme 4.1 Tautomerization of unstable trivalent phosphinous acids to the corresponding pentavalent secondary phosphine oxide

This tendency to obtain the secondary phosphorus oxide **99** tautomer as opposed to the phosphinous acid **98** could be seen as early as their first reported synthesis. In 1952, Williams and Hamilton were the first to document the synthesis of secondary phosphine oxides **99** or phosphinous acids **98** (Scheme 4.2).¹

Scheme 4.2 First reported synthesis of secondary phosphine oxides

They demonstrated that if they reacted di-*n*-butyl phosphite **100** with an appropriate Grignard reagent or by reacting dialkylphosphinyl chloride **101** with lithium aluminum

hydride, they could generate secondary phosphine oxides **99**. Infrared absorption studies confirmed their secondary phosphine oxide structure. A few years later, with the help of phosphorus NMR, ^{31}P - ^1H heteronuclear spin-spin coupling also substantiated that similar phosphorus compounds ($\text{R} = \text{esters}$) primarily existed in the oxide form ($\text{R}_2\text{P}(\text{O})\text{H}$) as well.^{2,3}

In 1960, Griffiths and Burg discovered something remarkable, the first genuine phosphinous acid that did not tautomerize to its corresponding phosphorus oxide.⁴ They found that if they treated the diphosphoxane **102** with HCl they were able to obtain the bis(trifluoromethyl)phosphinous acid **103** after a trap-to-trap condensation of the gaseous reaction mixture (Scheme 4.3). They confirmed its structure by infrared spectroscopy (with a very strong O-H stretching frequency at 3620 cm^{-1} and a P-O stretching at 854 cm^{-1}).⁵ Even though the synthesis of the phosphinous acid **103** is tedious and risky due to the fact that $(\text{CF}_3)_2\text{POH}$, $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$, and especially $(\text{CF}_3)_2\text{PCl}$ react violently with air, which could explain why only very few investigations have been reported, the findings are truly interesting.^{4,5,6}

Scheme 4.3 Synthesis of the first genuine phosphinous acid

The strong electron-withdrawing trifluoromethyl groups ($-\text{CF}_3$) withdraw electron density from the phosphorus, thus making the oxygen atom relatively more basic compared to the phosphorus atom, which results in the stabilization of the phosphinous

acid tautomer. Thus strong electronegative substituents can shift the equilibrium towards the phosphinous acid. But not all electron-withdrawing groups yield similar results.

In 1966, McQuiston et. al. postulated the synthesis of bis(pentafluorophenyl)phosphinous acid **105** by the hydrolysis of bis(pentafluorophenyl)chlorophosphine **104**.⁷

Scheme 4.4 McQuiston et. al. postulated synthesis of bis(pentafluorophenyl)phosphinous acid

Take note that hydrolysis of secondary monohalophosphines rarely gives the expected phosphinous acids but rather a disproportionation occurs to give the corresponding phosphines, and phosphonic acids, as can be seen with diphenylchlorophosphine (Scheme 4.5).⁸

Scheme 4.5 Typical hydrolysis reaction of secondary monohalophosphines

McQuiston et. al. were unable to assign any vibrational modes by infrared spectroscopy to identify if the compound was a phosphinous acid **105** or a phosphine oxide **106**.

Therefore they attempted to determine its structure based on the ¹H NMR spectrum.

The authors observed two signals in the ¹H NMR in deuterated chloroform (4.00ppm and 13.3 ppm) and predicted that when R = pentafluorophenyl, both tautomeric forms, the phosphinous acid **105** and phosphine oxide **106**, existed in solution (Scheme 4.6).

Scheme 4.6 Tautomerization of bis(pentafluorophenyl)phosphinous acid

But in 2005, nearly 40 years later, Hoge et. al. with experiments of their own, explain that the data that McQuistion et. al. collected was correct but the interpretation of the ^1H NMR was wrong.⁹ In fact, the two peaks that McQuistion et. al. recorded, was in fact a doublet ($^1J_{\text{PH}} = 558 \text{ Hz}$) corresponding to the phosphine oxide **106** tautomer. Through integration of the ^{31}P and ^{19}F NMR spectra, Hoge et. al. demonstrated that in toluene, dichloromethane, chloroform, and acetonitrile the compound exists in the tautomeric phosphine oxide **106** form, but in THF, ether, DMF, and DMSO the equilibrium could be pushed (but not completely) to the tautomeric phosphinous acid **105** form. X-ray crystallographic data of phosphine oxide **106** confirmed that it is the preferred tautomer in the solid state as well. Density functional theory (DFT) calculations performed by Hoge et. al. indicate that the bis(trifluoromethyl)phosphinous acid **103** is more stable than its corresponding phosphine oxide tautomer by 14 kJ/mol at the B3PW91/6-311G(3d,p), but that the bis(pentafluorophenyl)phosphinous acid **105** is only 1.7 kJ/mol (at the B3LYP/6-311G(2d,p) level) more stable than its corresponding phosphine oxide **106**. They suggest that it is this smaller energy difference between the tautomers which is why the bis(pentafluorophenyl)phosphinous acid **105** has a solvent dependent tautomeric equilibrium where as the bis(trifluoromethyl)phosphinous acid **103** does not.

In 1968, Chat and Heaton demonstrated that phosphinous acids **98** could be trapped by coordination to a transition metal center (in this particular case Pt) to obtain the complexed phosphinous acid **107** (Scheme 4.7).¹⁰

Scheme 4.7 Complexation of a phosphinous acid by a transition metal center

In 1975, Roundhill et. al. used this coordination displacement of the equilibrium to construct the platinum hybrid complex **110** by the reaction of tetrakis(triphenylphosphine)platinum complex **108** with diphenylphosphine oxide **109**.¹¹ An interesting detail in the coordination of the ligand is the intramolecular hydrogen bond in the backbone that forms a quasi-chelate, which adds a conformational stability to the complex **110**.

Scheme 4.8 Complexation of a phosphinous acid by a transition metal center

In the following years a plethora of transition metal complexed phosphinous acid derivatives were synthesized.^{12,13} In 1986, van Leeuwen et. al. for the first time demonstrated the catalytic potential of these phosphinous acid ligands, for Pt-catalyzed hydroformylation of hept-1-ene and hept-2-ene.^{14,15} In 1995, Parkins and Ghaffar demonstrated how similar Pt-catalysts were extremely active in catalyzing the

hydrolysis of nitriles to amides.¹⁶ But it wasn't until Li's 2001 report did the incorporation of phosphinous acid ligands for catalysis gain significant attention.

In 2001, Li reported the first synthesis of simple, readily available, air and moisture stable secondary phosphine oxides (SPOs) (Scheme 4.9).¹⁷ In his report he demonstrated how secondary phosphine oxides (SPOs) are extremely useful preligands (the ligand being the phosphinous acid coordinated to the transition metal) in Pd-catalyzed cross-coupling reactions of non-activated aryl chlorides. Once the phosphinous acid complex is deprotonated with a base (e.g. NaOR, Na₂CO₃, CsF) it yields an electronic-rich anionic compound that is utilized to facilitate the oxidative addition of aryl chlorides in homogeneous catalysis, which is the rate-limiting step. Usually the low catalytic reactivity of aryl chlorides in cross-coupling reactions is attributed to their unwillingness towards oxidative addition to Pd⁰.¹⁸ With these results, a new area of research in organometallic chemistry was born.

Scheme 4.9 Synthesis of air-stable phosphine oxide preligands and their corresponding phosphinous acid ligand complexes

After Li's report, a large amount of work began to focus on phosphinous acids and their proven significance as ligands for homogeneous and enantioselective catalysis. The subject has been highlighted in a report by Börner¹⁹, and reviews by Ackermann²⁰ and Hong et. al.²¹. One report by Martin, Buono, et. al. using a combination of experimentally measured and/or calculated CO stretching frequencies suggest that the inferred electronic properties of ligands stemming from secondary phosphine oxides span a

large range, going from π -accepting phosphite-like compounds to extremely electron-donating ligands outclassing N-heterocyclic carbenes.²²

It has been 60 years since Williams and Hamilton first reported the synthesis of secondary phosphine oxides and/or their phosphinous acid tautomer.¹ Since that time only 2 examples have been reported in the literature as true phosphinous acids and 1 as a close phosphinous acid derivative. The first was the bis(trifluoromethyl)phosphinous acid **103** by Griffiths and Burg in 1960 as previously mentioned.⁴ It should be mentioned that more recently Hoge et. al. described an easier and safer, one step, high yielding synthesis of the bis(trifluoromethyl)phosphinous acid **103**, by reacting the amino phosphine **111** with at least 3 equivalents of carefully dried *p*-toluenesulfonic acid (TosOH)(Scheme 4.10).

Scheme 4.10 Hoge et. al. improved synthesis of bis(trifluoromethyl)phosphinous acid

It should also be mentioned that with the improved synthesis of phosphinous acid **103** came an improved IR spectra of the gaseous sample²³ exhibiting two bands in the OH stretching region (3672 and 3598 cm^{-1}) rather than one at 3620 cm^{-1} as described by Griffiths and Burg^{4,5}. The two bands correspond to two rotational isomers: one where the OH group is oriented *cis* relative the C-P-C bisector and the other oriented *trans*, with the *cis* being more stable by 5.9 kJ/mol , and the energy difference between the *trans* phosphinous acid isomer and the phosphine oxide tautomer calculated to be 12.6 kJ/mol .²³

The second true phosphinous acid was synthesized recently in 2009, almost fifty years later, by Hoge et. al.. The bis(pentafluoroethyl)phosphinous acid **113** is synthesized from trifluoro[bis(heptafluoropropyl)]phosphorane **112** (Scheme 4.11).²⁴

Scheme 4.11 Synthesis of bis(pentafluoroethyl)phosphinous acid

The bis(pentafluoroethyl)phosphinous acid **113** gas-phase IR spectrum also exhibits two OH stretching modes (3666 and 3595 cm⁻¹) assigned to two rotational isomers with the OH either *cis* or *trans* to the C-P-C bisector. The calculated energy difference between the *cis* and *trans* conformers is 7.3 kJ/mol with the *cis* conformer being more stable. The *cis* and *trans* conformers of bis(pentafluoroethyl)phosphinous acid **113** are calculated to be more stable than the phosphine oxide tautomer by 11.7 and 4.4 kJ/mol, respectively. Recently Bader et.al. were able to obtain solid-state structures of bis(pentafluoroethyl)phosphinous acid **113**, as well as bis(trifluoromethyl)phosphinous acid **103**, confirming their phosphinous acid structure.²⁵

Finally, a close phosphinous acid derivative was reported in 2008, by Cowley et. al.. They synthesized a β -diketiminato hydroxyphosphenium cation **114** and found it to be more stable than its hydrophosphoryl tautomer **115** (Scheme 4.12).²⁶

Scheme 4.12 Equilibrium of a hydroxyphosphenium cation and its hydrophosphoryl tautomer

The absence of ^{31}P - ^1H coupling in the ^{31}P and ^1H NMR, the presence of OH stretch at 3364 cm^{-1} in the IR spectrum, as well as an X-ray crystallography all confirmed the structure as the hydroxyphosphenium cation tautomer **114**.

In a recent patent,²⁷ Hoge et. al. demonstrated that bis(pentafluoroethyl)phosphinous acid **113** reacts with PdCl_2 at room temperature to give mono **116** and dinuclear **117** complexes.

Scheme 4.13 Reaction of bis(pentafluoroethyl)phosphinous acid with PdCl_2 to give mono and dinuclear complexes

The patent goes on to describe the catalytic activity of complex **117** in Suzuki coupling reactions. Using a catalyst loading of 0.004 mol%, after 20 hours at room temperature they obtained a 98% conversion (TON 24500) (Scheme 4.14).

Scheme 4.14 Suzuki coupling reaction using complex **117** as the catalyst

This example highlights the potential in finding new stable phosphinous acids and exploring their use in homogenous catalysis. In this work we will attempt to generate the unknown terminal hydroxyphosphinidene and trap it with several substrates (i.e. alkynes, alkenes, etc.) to yield a variety of new complexed phosphinous acids which will be decomplexed to give free phosphinous acids (Scheme 4.15).

Scheme 4.15 General reaction scheme for using terminal hydroxyphosphinidenes as a source for new phosphinous acids

4.2 Results and discussion

Since it is difficult to imagine the synthesis of hydroxyphosphinidene complexes from any other route we will use the original and still most useful approach, the 7-phosphanorbornadiene method devised by Mathey et. al. (Scheme 4.16).²⁸

Scheme 4.16 The 7-phosphanorbornadiene approach for generating terminal phosphinidenes

In practice, this means that the straightforward method to the hydroxyphosphinidene must begin with the synthesis of the presently unknown 1-hydroxyphospholes. Before beginning our experiments we decided to perform some DFT calculation to see whether the equilibrium lies toward the 1-hydroxyphosphole or toward the phosphole oxide. It should be mentioned that calculations have shown that the oxidation of the phosphorus atom in phospholes increases its anti-aromatic character²⁹, as well as the fact that phosphole oxides tend to dimerize via a [4+2] cycloaddition³⁰. Thus, knowing in which way the equilibrium lies is a crucial question for the feasibility of this approach. We computed by DFT the structures and energies of the two tautomers at the B3LYP/6-311+G(d,p) level. The structural results are shown in figure 4.1

Figure 4.1 Computed structures of 1-hydroxyphosphole **118** and phosphole oxide **119**.

Selected distances (Å) and angles (deg.). **118**: C1–P9 1.816, C1–C2 1.349, C2–C3 1.4771; C1–P–O 106.6°. **119**: C1–P10 1.825, C1–C2 1.340, C2–C3 1.485; C1–P–C4 91.9°, C1–P–O9 120.9°, C1–P–H11 102.4°.

The data clearly shows the destabilization in the structure of **119** with longer P–C bonds and less delocalization within the dienic system compared to **118**. But one of the most important result concerns the difference in energy: the phosphinous acid **118** is more stable than the phosphole oxide **119** by 3.61 kcal/mol (or 15.12 kJ/mol) (ZPE-corrected energy included). Meanwhile the bis(trifluoromethyl)phosphinous acid **103** is calculated to be 3.35 kcal/mol (or 14.4 kJ/mol) (ZPE corrected) more stable than its phosphine oxide tautomer.²⁴ In the case of the bis(trifluoromethyl)phosphinous acid **103** it is the lower basicity of the phosphorus due to the strong electron-withdrawing trifluoromethyl groups (–CF₃) that stabilizes the phosphinous acid tautomer. In the case of the phosphinous acid **118** it is the anti-aromatic character of the phosphine oxide **119** that stabilizes the phosphinous acid tautomer.

We also performed a DFT study of the hydroxyphosphinidene pentacarbonylchromium complex and its tautomer the phosphinidene oxide pentacarbonylchromium complex.

Figure 4.2 Computed structures at the B3LYP/6-31G(d) (C,H,O,P) and lanl2sz (Cr) level of hydroxyphosphinidene and phosphinidene oxide $\text{Cr}(\text{CO})_5$ complexes. Selected distances ($\text{\AA}$) and angles (deg.). **120**: P–Cr 2.237, P–O 1.661, O–H 0.973; O–Cr–P 109.4°. **121**: P–Cr 2.252, P–O 1.497, P–H 1.439; O–P–Cr 133.2°, O–P–H 107.3°, H–P–Cr 119.5°.

A key point is that the phosphinidene oxide $\text{Cr}(\text{CO})_5$ **121** appears to be more stable than the phosphinous acid $\text{Cr}(\text{CO})_5$ **120** by 11.09 kcal/mol (or 46.42 kJ/mol) (ZPE included). Thus the stabilization of hydroxyphosphinidene complexes by tautomerization appears likely. But of course, the extent of this stabilization will depend on the complexing group. Furthermore, even though hydroxyphosphinidene complexes may reach stability through prototropy, it does not mean that they cannot be trapped. There is also the question of the activation barrier between the two tautomers and if it will slow down the transformation into the phosphinidene oxide.

Finally we performed comparative DFT calculation of the 1-hydroxyphosphirane, 1-hydroxyphosphirene, as well as their phosphine oxide counterparts. The results were original and very interesting. At the B3LYP/6-311+G(d,p) level, the phosphinous acids of the phosphirane and phosphirene appear to be more stable than their phosphine oxide tautomers by 13.24 kcal/mol (or 55.38 kJ/mol) (ZPE included) and 13.50

kcal/mol (or 56.47 kJ/mol) (ZPE included), respectively. Thus they are by far the most stable phosphinous acid derivatives potentially accessible.

Scheme 4.17 In both the phosphirane (left) and phosphirene (right) cases the phosphinous acid is predicted to be the most stable tautomer.

We first attempted to synthesize the unknown 1-hydroxyphospholes by reacting 1-cyano-2,3-dimethylphosphole³¹ by controlled hydrolyses, but unfortunately our preliminary attempts failed. Whether the reactions failed due to the intrinsic instability of the 1-hydroxyphospholes or in the incompatibility of our synthetic approach, we thus decided to work directly in the coordination sphere of the group VI transition metals. Our newly improved synthesis of 1-chlorophosphole pentacarbonyltungsten complex **70** seemed like an excellent starting point.³²

We first started by heating 1-chloro-3,4-dimethylphosphole tungsten complex **70** with water to find that it undergoes a simple hydrolysis to the 1-hydroxy-3,4-dimethylphosphole tungsten complex **122**. A minor product was isolated from this reaction but it will be discussed in the following chapter.

Scheme 4.18 Synthesis of 1-hydroxy-3,4-dimethylphosphole tungsten complex

It should be mentioned that the 1-hydroxy-3,4-dimethylphosphole tungsten complex **122** has been detected by ³¹P NMR before but never fully characterized.³¹ We have

characterized the phosphinous acid complex **122** as well obtained its X-ray crystal structure (Figure 4.3).

Figure 4.3 X-ray crystal of 1-hydroxy-3,4-dimethylphosphole tungsten complex. Selected bond lengths (Å) and angles (deg): P1–W1 2.4792(12), P1–O6 1.617(3), P1–C6 1.798(5), C6–C7 1.336(7), C7–C9 1.495(7), C9–C11 1.333(7), P1–C11 1.794(5); W1–P1–O6 109.97(13)°, C6–P1–C11 91.0(2)°. Ellipsoids drawn at 50% probability level.

Next we reacted the 1-hydroxy-3,4-dimethylphosphole with DMAD and obtained the 7-hydroxy-7-phosphanorbornadiene complex **123**. Its X-ray crystal structure can be seen in figure 4.4.

Scheme 4.19 Synthesis of 7-hydroxy-7-phosphanorbornadiene tungsten complex

Figure 4.4 X-ray crystal of 7-hydroxy-7-phosphanorbornadiene tungsten complex. Selected bond lengths (Å) and angles (deg): P1–W1 2.4660(3), P1–O6 1.6032(8), P1–C6 1.8789(10), P1–C11 1.8858(10), C6–C7 1.5220(14), C7–C9 1.3416(15), C9–C11 1.5273(14), C11–C12 1.5121(12), C12–C13 1.3488(12); W1–P1–O6 108.18(3)°, C6–P1–C11 79.40(4)°, C6–P1–W1 125.27(3)°, C11–P1–W1 123.88(3)°, C6–P1–O6 107.90(4)°, C11–P1–O6 109.01(4)°. Ellipsoids drawn at 50% probability level.

It is interesting to note the temperature and reaction time that it takes to obtain the 7-hydroxy-7-phosphanorbornadiene tungsten complex **123** (60°C, 1 hour 15 min). In comparison, the methyl and phenyl phosphole tungsten complexes require much higher temperatures and reaction times to obtain their corresponding 7-phosphanorbornadiene (R = Me reaction with DMAD, 85-90°C for 15h; R = Ph reaction with DMAD, 85-90°C for 24h).³³ The high electronegativity of oxygen switches off the hyperconjugation between the diene and the exocyclic P–OH bond, therefore sharply

increasing the reactivity of the diene system. This is supported by DFT calculations as well as experimental evidence based on the reactivity of alkoxyphospholes.^{34,35}

In the process of optimizing the conditions for obtaining the 7-hydroxy-7-phosphanorbornadiene tungsten complex **123**, we found that a step-wise one-pot synthesis could be used to increase the overall yield. First, the chlorophosphole tungsten complex **70** is heated in a THF/water solution until the hydroxyphosphole tungsten complex **122** has been formed (by ^{31}P NMR). Next, without purifying complex **122** it suffices to merely remove the water from the reaction by pipette, add DMAD, and heat to obtain complex **123** (Scheme 4.20).

Scheme 4.20 Step-wise one-pot synthesis of 7-hydroxy-7-phosphanorbornadiene tungsten complex

We first attempted to trap the hydroxyphosphinidene complex **124** in the presence of alkynes. Heating at 70°C for 2 hours in the presence of diphenylacetylene (a.k.a. tolan) we were able to generate the hydroxyphosphinidene complex **124** and subsequently trap it to form the 1-hydroxyphosphirene complex **125** (Scheme 4.21). We were unable to cleanly isolate the minor product **126** at $^{31}\text{P } \delta = +147.6$

Scheme 4.21 Trapping of the hydroxyphosphinidene with diphenylacetylene to give the 1-hydroxyphosphirene complex

Next we heated the 7-hydroxy-7-phosphanorbornadiene tungsten complex **123** in the presence of cyclohexene, but unfortunately the reaction was not very clean. Within 1 hour of heating at 70°C, most of the starting material had been consumed with the appearance of several peaks in the +100 to +170 region (^{31}P NMR), the most prominent being at $^{31}\text{P } \delta = +147.6$ (complex **126**) and a trace peak at $^{31}\text{P } \delta = -41.6$, which we believe corresponds to the phosphirane complex **127** (Scheme 4.22). Heating for another hour at 70°C resulted in decomposition (i.e. a drastic decrease in signal-to-noise ratio). Attempts to isolate the products from the reaction by column chromatography (-10°C) were unsuccessful.

Scheme 4.22 Attempt to trap the hydroxyphosphinidene with cyclohexene to give the 1-hydroxyphosphirane

Next, we attempted to trap the hydroxyphosphinidene **124** with 2,3-dimethyl-1,3-butadiene to give the corresponding 1-hydroxyphospholene complex **129**. Within 2.5 hours at 70°C, by ^{31}P NMR, the starting material had been consumed and the signal-to-noise ratio drastically decreased (decomposition) as well as the appearance of several peaks in the +100 to +170 region (^{31}P NMR), including a peak at ^{31}P δ = +147.6 (complex **126**) (Scheme 4.23).

Scheme 4.23 Attempt to trap the hydroxyphosphinidene with 2,3-dimethyl-1,3-butadiene to give the 1-hydroxyphospholene

We soon began to wonder if the hydroxyphosphirane and hydroxyphospholene were too unstable at 70°C. After all, phosphiranes are known to be less stable than phosphirenes (as mentioned in chapter 1). Previous work has shown CuCl to catalyze the breaking of the 7-methoxy-7-phosphanorbornadiene tungsten complex to generate the methoxyphosphinidene at 55°C.³⁶ Consequently, it should also catalyze the breaking of the 7-hydroxy-7-phosphanorbornadiene complex **123** and thus form the hydroxyphosphinidene **124** at lower temperatures, perhaps decreasing the amount side reactions.

We then reacted the 7-hydroxy-7-phosphanorbornadiene complex **123** with cyclohexene and CuCl at 55°C. Within 2 hours all the starting material had been

consumed. Unfortunately the reaction produced several products with peaks in the +100 to +150 region (^{31}P NMR), including the unidentified complex **126**, as well as (this time in minor amounts instead of trace) two peaks at ^{31}P $\delta = -23.7$ and -41.6 which we believe correspond to the two possible isomers of complex **127**. Attempts to isolate the products from the reaction by column chromatography (-10°C) were unsuccessful

When we reacted the 7-hydroxy-7-phosphanorbornadiene complex **123** with 2,3-dimethyl-1,3-butadiene and CuCl , after 2 hours at 55°C , the ^{31}P NMR spectrum had a drastic decrease in the signal-to-noise ratio, as well as, several products present. The largest peak was the complex **126**, followed by unreacted starting material, several small peaks in the ^{31}P $\delta = +100$ to $+170$ region, as well as two small peaks, one at ^{31}P $\delta = -22.8$ and another at ^{31}P $\delta = +112.0$ ($1J_{\text{PW}} = 264$ Hz), which we believe to correspond to the phosphirane complex **128** and the hydroxyphospholene complex **129**. After 2 more hours the starting material was consumed and compound **126** ^{31}P $\delta = +147.6$ ($1J_{\text{PW}} = 318$ Hz) was observed as the major product accompanied by many minor peaks in the ^{31}P NMR ($\delta = +100$ to $+170$), as well as a minor peak at ^{31}P $\delta = +112.0$ ($1J_{\text{PW}} = 264$ Hz), which we believe to be the hydroxyphospholene **129**. Unfortunately, attempts to isolate the products from the reaction by column chromatography (-10°C) were unsuccessful.

Scheme 4.24 Trapping of the hydroxyphosphinidene complex with 2,3-dimethyl-1,3-butadiene to obtain the hydroxyphosphirane **128** which would then undergo ring expansion to the hydroxyphospholene **129**.

The problem with these trapping reactions was that several side reactions were taking place. The most significant was the formation of the unknown complex **126**. We

performed several tests where we heated the 7-hydroxy-7-phosphanorbornadiene complex **123** in the absence of trapping reagents and found that the unknown complex **126** was still produced, but we were unable to isolate it in pure form.

Later on, our group started investigating thiolyphospholes and their chemistry, some of which will be discussed in the following chapter. Lin and Mathey performed several reactions with thiolyphosphole and DMAD and were able to isolate a side product, complex **130**, that also appeared in several of their reactions (Scheme 4.25).³⁷ What they had discovered was that the S–H bond was adding across the activated C=C double bond to make the 7-phosphanorbornene complex **130**.

Scheme 4.25 Lin and Mathey's 7-phosphanorbornene complex **130** which is the result of the S–H bond adding across the activated C=C double bond

We believe the product they isolated and ultimately confirmed by X-ray crystallography is the sulfur analogue of our unknown complex **126**. In our case, we believe that at elevated temperatures the O–H bond adds across the activated C=C double bond as well, resulting in the formation of complex **126**, and thereby consuming most of the starting material needed for generating the hydroxyphosphinidene **124**.

Terminal phosphinidene complexes are known to formally insert into the O–H bonds of alcohols to generate secondary phosphine complexes.²⁸ Attempts to trap the hydroxyphosphinidene **124** with alcohols, such as methanol and phenol, were attempted next but were unsuccessful due to the formation of several products whose major products were difficult to purify and often did not contain a P–H bond (^{31}P – ^1H

NMR) indicating that they were not the desired products. Attempts to isolate the products from the reaction by column chromatography (-10°C) were unsuccessful.

Due to the increased polarity (P–OH) of the products in several of these trapping reactions, the products were often difficult to separate from the unavoidable phthalate **3** byproduct, which serves as the driving force for generating the terminal phosphinidene (an occasional problem that can arise, as mentioned in chapter 1). Another reason why the isolation of many of the products failed was due to the instability of the compounds during chromatography (even at low temperature).

Now that we understood that the O–H bond could be adding across the C=C double bond of the 7-hydroxy-7-phosphanorbornadiene complex **123** at elevated temperatures, we wondered if we could protect the OH group for example by trimethylsilane. We reacted the 7-hydroxy-7-phosphanorbornadiene complex **123** with triethylamine followed by chlorotrimethylsilane (TMSCl) at 0°C to form the 7-trimethylsiloxy-7-phosphanorbornadiene complex **131** (Scheme 4.26).

Scheme 4.26 Formation of the 7-trimethylsiloxy-7-phosphanorbornadiene complex

Complex **131** is very susceptible to hydrolysis, giving back the 7-hydroxy-7-phosphanorbornadiene **123**, thus care must be taken to avoid moisture, as well as avoiding its contact with silica and alumina gel.

Attempts to heat the 7-trimethylsiloxy-7-phosphanorbornadiene complex **131** with diphenylacetylene to trap the trimethylsiloxyphosphinidene were unsuccessful.

Unlike the 7-hydroxy-7-phosphanorbornadiene complex **123** which would collapse around 70°C, complex **131** needed much higher temperatures to collapse the phosphorus bridge, with the collapse starting around 110-120°C. Over time at such high temperature the reaction resulted in decomposition. We attempted to use CuCl as a catalyst to reduce the temperature needed to break the bridge, but the CuCl was ineffective. It appears that in the presence of silanes, CuCl is ineffective at catalyzing the collapse of the phosphorus bridge.

Even though attempts to trap the hydroxyphosphinidene **124** to make several other phosphinous acid tungsten complexes had proven unsuccessful; we still had the 1-hydroxyphosphirene complex **125**. Next, we attempted to decomplex the tungsten to obtain the free phosphinous acid. There are two common techniques for decomplexing tungsten from phosphorus. The first, involves reacting the phosphorus tungsten complex with iodine followed by *N*-methylimidazole in dichloromethane.³⁸ The iodine oxidizes the tungsten and the phosphorus ligand is then displaced by the *N*-methylimidazole. Unfortunately this technique was unsuccessful for decomplexing the hydroxyphosphirene complex **125** and we were left with nothing but decomposition.

The second technique involves the displacement of the metal from phosphorus by a bidentate ligand such as 2-bis(diphenylphosphino)ethane (dppe).^{39,40} When we heated the hydroxyphosphirene complex **125** with dppe, no reaction occurred until around 115°C. Heating the starting material for 1 hour at 115°C led to loss of **125** (by ³¹P NMR) and led to decomposition. Whether the free phosphinous acid of complex **125** is unstable at such high temperatures, or merely these techniques are unsuitable for this particular decomplexation; more milder decomplexing techniques need to be discovered and explored.

4.3 Conclusion

Phosphinous acids are unstable and readily rearrange to their secondary phosphine oxide counterpart. Only two genuine phosphinous acids have been synthesized that do not rearrange to the phosphine oxide, the bis(trifluoromethyl)phosphinous acid **103** and the bis(pentafluoroethyl)phosphinous acid **113**. Numerous publications have demonstrated phosphinous acids to be useful ligands for homogeneous and enantioselective catalysis. Thus proving them as interesting synthetic targets. In this work we are attempting to use the hydroxyphosphinidene complex as a source of new phosphinous acids after tungsten decomplexation. We successfully trapped the hydroxyphosphinidene with alkynes, such as diphenylacetylene to give the hydroxyphosphirene tungsten complex **125**. Our attempts to decomplex the tungsten from the hydroxyphosphirene complex were unsuccessful. This is unfortunate, because our DFT calculations predict the hydroxyphosphirene to be the most stable phosphinous acid derivative potentially accessible. Thus more work needs to be done in researching milder decomplexation methods.

Our attempts to synthesize and isolate other phosphinous acids by trapping the hydroxyphosphinidene with other substrates (i.e. butadienes, alkenes, alcohols) have proven unsuccessful in part to three main reasons. The first is based on work done by Lin and Mathey, which suggests that the O–H bond adds across the reactive double bond in the 7-hydroxy-7-phosphanorbornadiene complex thus reducing the efficiency of the generation of the hydroxyphosphinidene precursor due to this unwanted side reaction. The second is due to the fact that some of the phosphinous acid complexes are unstable, at the temperatures at which the hydroxyphosphinidene is generated, as well, upon chromatography. Reason number three, due to the increased polarities of the products,

attempts to separate the products (expected or unexpected) from the phthalate **3** byproduct often proves difficult.

Now that we understand more of what is occurring in these reactions, we can begin to devise new strategies for generating hydroxyphosphinidenes as well as to look for new decomplexing methods that are milder and efficient to obtain the free hydroxyphosphirene as well as other interesting organophosphorus compounds.

4.4 Experimental

Toluene was dried before use. Silica gel (230-400 mesh) was used for the chromatographic separations. NMR spectra were recorded on either a JEOL ECA 400, or JEOL ECA 400SL spectrometer. All spectra were recorded at 298K in CD₂Cl₂ unless otherwise specified. HRMS spectra were obtained on a Water Q-ToF Premier MS. X-ray crystallographic analyses were performed on a Bruker X8 APEX diffractometer. All reactions were performed under argon. All commercially available reagents were used as received from the suppliers.

1-Hydroxy-3,4-dimethylphosphole tungsten complex 122

1-Chloro-3,4-dimethylphosphole tungsten complex (2.00g, 4.25mmol), THF (18mL), and D.I. water (16mL) were added to a Schlenk under argon. The reaction mixture was heated for 2 hours at 60°C. The reaction mixture was then transferred to a separatory funnel and the organic mixture was extracted using methylene chloride. Next the organic layer was dried with MgSO₄ and filtered. The solvent was subsequently removed under vacuum and the crude product was purified by column chromatography (0°C) on silica gel with methylene chloride as the eluent (R_F = 0.38), solvent was then removed under vacuum, to give a whitish-yellow solid (1.38g, 71.8% yield).

³¹P NMR (CD₂Cl₂) δ 103.2 (¹ J_{PW} = 256 Hz); ¹H NMR (CD₂Cl₂): δ 2.09 (d, J = 0.9 Hz, 6H, CH₃), 3.30 (broad s, 1H, OH), 6.20 (dd, ² J_{HP} = 37.0 Hz, J = 0.9 Hz, 2H, C=C-H); ¹³C NMR (CD₂Cl₂) δ 16.98 (d, J = 12.3 Hz, CH₃), 128.99 (d, ¹ J_{CP} = 43.1 Hz, =C-H), 150.44 (d, ² J_{CP} =

12.3 Hz, =C-Me), 196.31 (d, $^2J_{\text{CP}} = 7.4$ Hz, *cis*-CO), 199.57 (d, $^2J_{\text{CP}} = 20.9$ Hz, *trans*-CO).

HRMS m/z 451.9646 (calcd for $\text{C}_{11}\text{H}_9\text{O}_6\text{P}^{184}\text{W}$, 451.9644).

7-Hydroxy-7-phosphanorbornadiene complex 123

Method 1:

1-Hydroxy-2,3-dimethylphosphole tungsten complex (0.2438g, 0.539mmol), dimethyl acetylenedicarboxylate (0.5mL, 4.07mmol), and THF (3mL) were added to a Schlenk under argon. The reaction mixture was heated for 1 hour 15 min at 60°C. The solvent was subsequently removed under vacuum and the crude product was purified by column chromatography (0°C) on silica gel with methylene chloride as the eluent ($R_F = 0.18$), or if necessary 98:2 methylene chloride: acetone mixture, solvent was then removed under vacuum, to give a whitish-yellow solid (0.199g, 62.2% yield).

Method 2 (step-wise one-pot):

1-Chloro-3,4-dimethylphosphole tungsten complex (3.22g, 6.84mmol), THF (30mL), and D.I. water (30mL) were added to a Schlenk under argon. The reaction mixture was heated for 2 hours at 60°C. Next the Schlenk was cooled in an ice bath and the aqueous layer (colorless) was removed by pipette. Next dimethyl acetylenedicarboxylate (1.5mL, 12.2mmol) was added and the reaction was heated for 2 hours at 60°C under argon. The solvent was subsequently removed under vacuum and the crude product was purified by column chromatography (0°C) on silica gel with methylene chloride as the eluent ($R_F = 0.18$), or if necessary 98:2 methylene chloride: acetone mixture, solvent was then removed under vacuum, to give a whitish-yellow solid (2.40g, 59.0% yield).

^{31}P NMR (CD_2Cl_2) δ 209.0 ($^1J_{\text{PW}} = 271$ Hz); ^1H NMR (CD_2Cl_2): δ 2.00 (d, $J = 1.4$ Hz, 6H, CH_3), 3.80 (s, 2H, P-C-H), 3.81 (s, 6H, C-OMe), 7.2 (broad s, 1H, O-H); ^{13}C NMR (CD_2Cl_2) δ 16.19 (s, C- CH_3), 53.27 (s, O- CH_3), 64.19 (d, $^1J_{\text{CP}} = 13.6$ Hz, P-C-H), 135.06 (d, $^2J_{\text{CP}} = 20.9$ Hz, =C-Me), 143.15 (d, $^2J_{\text{CP}} = 4.9$ Hz, =C- CO_2Me), 165.99 (d, $^3J_{\text{CP}} = 2.4$ Hz, - CO_2Me), 195.85 (d, $^2J_{\text{CP}} = 8.6$ Hz, *cis*-CO), 198.26 (d, $^2J_{\text{CP}} = 30.8$ Hz, *trans*-CO). HRMS m/z 592.9883 (calcd for $\text{C}_{17}\text{H}_{15}\text{O}_{10}\text{P}^{183}\text{W}$, 592.9905).

1-Hydroxyphosphirene complex 125

7-Hydroxy-7-phosphanorbornadiene tungsten complex (0.114g, 0.192mmol), diphenylacetylene (0.158g, 0.884mmol), and toluene (4mL) were added to a Schlenk under argon. The reaction mixture was heated for 2 hours at 70°C. The solvent was subsequently removed under vacuum and the crude product was purified by column chromatography (0°C) on silica gel with methylene chloride as the eluent ($R_F = 0.28$), solvent was then removed under vacuum, to give a whitish-yellow solid (0.0303g, 29% yield).^{41,42}

^{31}P NMR (CD_2Cl_2) δ -80.2 ($^1J_{\text{PW}} = 316$ Hz); ^1H NMR (CD_2Cl_2): δ 3.40 (broad s, 1H, -OH), 7.50-7.63 (m, 6H, Ph-H), 7.93-7.96 (m, 4H, Ph-H); ^{13}C NMR (CD_2Cl_2) δ 128.37 (d, $J_{\text{CP}} = 4.9$ Hz, Ph), 129.86 (s, Ph), 130.52 (d, $J_{\text{CP}} = 4.9$ Hz, Ph), 131.58 (s, Ph), 148.26 (d, $^1J_{\text{CP}} = 15.8$ Hz, P-C=), 196.02 (d, $^2J_{\text{CP}} = 9.7$ Hz, *cis*-CO), 199.33 (d, $^2J_{\text{CP}} = 38.8$ Hz, *trans*-CO). HRMS m/z 549.9793 (calcd for $\text{C}_{19}\text{H}_{11}\text{O}_6\text{P}^{184}\text{W}$, 549.9803).

7-Trimethylsiloxy-7-phosphanorbornadiene complex 131

7-Hydroxy-7-phosphanorbornadiene tungsten complex (0.200g, 0.337mmol) was dissolved in dry methylene chloride (3mL) in a Schlenk under argon. Next the reaction mixture was placed in an ice bath and triethylamine (0.14mL, 1.00mmol) was added dropwise at 0°C. The reaction was stirred for 5 min at 0°C. Next chlorotrimethylsilane (0.13mL, 1.00mmol) was added dropwise to the reaction mixture at 0°C. Once the addition was complete the reaction was allowed to warm-up to room temperature. The solvent and any excess reagents were subsequently removed under vacuum and the reaction mixture was then dissolved in dry toluene. The product in toluene was then filtered through magnesium sulfate under argon. Finally the solvent was removed under vacuum to give a yellow solid (0.210g, 94% yield).

^{31}P NMR (CD_2Cl_2) δ 201.4 ($^1J_{\text{PW}} = 274$ Hz); ^1H NMR (CD_2Cl_2): δ 0.24 (s, 9H, $-\text{Si}(\text{CH}_3)_3$), 1.99 (d, $J = 1.8$ Hz, 6H, $=\text{C}-\text{CH}_3$), 3.75 (s, 2H, P-C-H), 3.78 (s, 6H, $-\text{OCH}_3$); ^{13}C NMR (CD_2Cl_2) δ 1.37 (s, $-\text{Si}(\text{CH}_3)_3$), 16.27 (s, $-\text{CH}_3$), 52.73 (s, $-\text{OCH}_3$), 65.40 (d, $^1J_{\text{CP}} = 13.6$ Hz, P-C-H), 135.38 (d, $^2J_{\text{CP}} = 23.4$ Hz, $=\text{C}-\text{Me}$), 143.34 (d, $^2J_{\text{CP}} = 4.9$ Hz, $=\text{C}-\text{CO}_2\text{Me}$), 165.67 (d, $^3J_{\text{CP}} = 3.7$ Hz, $-\text{CO}_2\text{Me}$), 196.58 (d, $^2J_{\text{CP}} = 8.7$ Hz, *cis*-CO), 198.48 (d, $^2J_{\text{CP}} = 32.0$ Hz, *trans*-CO). HRMS m/z 666.0291 (calcd for $\text{C}_{20}\text{H}_{23}\text{O}_{10}\text{PSi}^{184}\text{W}$, 666.0308).

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CHAPTER 5

Intramolecular [4+2] *Versus* [2+2] Cycloadditions in P–X–P-Linked Biphospholes (X = O, S)

5.1 Introduction

It has been known for quite some time that the phosphole ring has a tendency to dimerize via a [4+2] cycloaddition whenever the phosphorus lone pair is oxidized or complexed.^{1,2,3,4} This dimerization heavily depends on two factors. The first is the substitution pattern of the ring. If the substitution is low,^{5,6,7,8} the phosphole oxides are so reactive that they instantly dimerize to give the [4+2] endo dimers (Scheme 5.1).

Scheme 5.1 The rapid dimerization by a [4+2] cycloaddition of low substituted phospholes

If the substitution is high such as pentasubstituted phosphole oxides^{9,10,11,12} then they are stable as monomers. The 1,2,5-triphenylphosphole oxide¹³ is also stable as the monomer, most likely due to partial stabilization through conjugation with the 2,5-diphenyl substituents.

The second factor that the dimerization heavily depends on is the nature of the substitution at phosphorus. The classical examples being the reactivities of the 1-phenyl-3,4-dimethylphosphole oxide **131** and sulfide **133**. The oxide **131** dimerizes upon standing at room temperature (or rapidly upon heating) to give the oxide dimer

132 (Scheme 5.2).^{14,15} The sulfide **133**, however, needs prolonged heating in boiling xylene to slowly form the dimer **134** (Scheme 5.3).¹⁶

Scheme 5.2 The dimerization of 1-phenyl-3,4-dimethylphosphole oxide

Scheme 5.3 The dimerization of 1-phenyl-3,4-dimethylphosphole sulfide

The [2+2] dimerization, on the contrary, is not very well known. A representative example, by Mathey et. al., relies on the UV irradiation of a *cis*-(phosphole)₂Mo(CO)₄ complex to give the [2+2] dimer (Scheme 5.4).¹⁶

Scheme 5.4 A [2+2] dimerization of a *cis*-(phosphole)₂Mo(CO)₄ complex

Nelson et. al. have seen a few [2+2] dimers using *cis*-bis(phosphole) complexes of ruthenium¹⁷ and palladium¹⁸, but other products were always obtained in addition, such

as the [4+2] dimerization as well as other products in the palladium case. Often the product ratios would vary depending on the auxiliary ligands on the transition metal. We wish to report here on a new case in which a minor change in the structure of the P-X-P-linked biphosphole derivative leads to a complete shift from the [4+2] to the [2+2] dimerization.

5.2 Results and discussion

During our experiments to obtain the 1-hydroxyphosphole tungsten complex **122**, we isolated a very minor product, the dimeric oxide complex **135**.

Scheme 5.5 Formation of the 1-hydroxyphosphole tungsten complex resulted in a minor formation of a dimeric oxide complex

This complex has been seen and isolated before during the synthesis of 1-fluoro-3,4-dimethylphosphole complex **65**. Mathey et. al. found that when they used wet KF in the synthesis of complex **65** they obtained the dimeric oxide complex **135** as the major product (Scheme 5.6).¹⁹ They did not detect the P-O-P-linked biphosphole complex **137** intermediate by NMR. Recently we decided to reinvestigate its synthesis, as well as, look at the properties of its sulfur analogue.

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Scheme 5.6 Synthesis of the 1-fluoro-3,4-dimethylphosphole complex and the dimeric oxide complex from the 1-chloro-3,4-dimethylphosphole complex

The perfect starting points were our 1-hydroxy-3,4-dimethylphosphole tungsten complex **122** and our 1-chloro-3,4-dimethylphosphole tungsten complex **70**. We first deprotonated the 1-hydroxy-3,4-dimethylphosphole tungsten complex **122** with a mild base (*N*-methylimidazole) to give the phosphorus anion **136**. Next, 1-chloro-3,4-dimethylphosphole complex **70** was added at 0°C to give the P-O-P-linked biphosphole complex **137** (Scheme 5.7).

Scheme 5.7 Synthesis of the P-O-P-linked biphosphole complex

Care must be taken with complex **137** because even at room temp it begins to undergo the [4+2] cycloaddition to give the dimeric oxide complex **135** and much more quickly at higher temperatures (Scheme 5.8). This explains why Mathey et. al. were unable to previously detect the P-O-P-linked biphosphole complex **137**.

Scheme 5.8 [4+2] Cycloaddition of the P-O-P-linked biphosphole complex to give the dimeric oxide complex

Around this time we began investigating the sulfur analogues of complex **122** and **137**. Starting from the known sulfur anion complex **138**,²⁰ we added trifluoroacetic acid at $0^\circ C$ to obtain the 1-thiolyphosphole complex **139**. Its X-ray crystal structure can be seen in figure 5.1.

Scheme 5.9 Synthesis of 1-thioly-3,4-dimethylphosphole tungsten complex

Figure 5.1 X-ray crystal of 1-thioly-3,4-dimethylphosphole tungsten complex. Selected bond lengths (Å) and angles (deg): P1–W1 2.4832(6), P1–S1 2.1087(9), P1–C6 1.791(2), P1–C11 1.794(2), C6–C7 1.342(4), C7–C10 1.487(4), C10–C11 1.344(3); P1–S1–H 96(2)°, W1–P1–S1 114.14(3)°, C6–P1–S1 100.83(9)°, C6–P1–C11 91.63(12)°, C11–P1–S1 106.89(9)°. Ellipsoids drawn at 50% probability level.

Next, we synthesized the P–S–P-linked biphosphole complex **140** by reacting the sulfur anion complex **138** with 1-chloro-3,4-dimethylphosphole tungsten complex **70** at room temperature (Scheme 5.10). Its X-ray structure can be seen in figure 5.2.

Scheme 5.10 Synthesis of the P–S–P-linked biphosphole tungsten complex

Figure 5.2 X-ray crystal structure of P–S–P-linked biphosphole tungsten complex. Selected bond lengths (Å) and angles (deg): P1–S1 2.064(2), S1–P2 2.080(2), P1–W1 2.4706(14), P2–W2 2.4696(14); P1–S1–P2 116.02(9). Ellipsoids drawn at 50% probability level.

Most likely due to the steric repulsion between the two bulky $\text{W}(\text{CO})_5$ complexing groups, the two phosphole rings of **140** stand face to face and are almost parallel: with an interplane angle of 14.14° . The sample crystals of complex **140** that was submitted for X-ray analysis was pure by ^{31}P NMR, but what we observed by X-ray diffraction was a mixture of complex **140** and the [2+2] dimer **141**. The X-ray structure of the [2+2] dimer can be seen in figure 5.3. The two isomers existed in the crystal in a ratio of 0.72/0.28 with the [2+2] dimer being the minor isomer.

When comparing the structures of **140** and **141**, the extreme distortion of the P–S–P bridge can easily be noticed. The P–S–P angle is reduced from 116° to 96° and P–S bonds are elongated from 2.06 to 2.36 Å. Thus, there is strain present in the [2+2] dimer **141**. Nevertheless, we observed that the P–S–P biphosphole **140** is spontaneously, although slowly, transformed into the [2+2] dimer at room temperature under visible light. If complex **140** is kept in the dark, the transformation is blocked. We tried heating complex **140** in the dark to see if it would produce the expected [4+2]

dimer, but we never observed its formation. At 100°C, complex **140** begins to decompose.

Figure 5.3 X-ray crystal structure of the [2+2] dimer of the P-S-P biphosphole. Selected bond lengths (Å) and angles (deg.): P1-S1A 2.375(5), S1A-P2 2.349(6), C23-C33 1.49(3), C23-C24 1.53(3), C23-P1 1.802(19), C24-C32 1.56(3), C32-C33 1.57(3); P1-S1A-P2 96.15(18)°. Ellipsoids drawn at 50% probability level.

Once it is formed, complex **141** again isomerizes, slowly at room temperature, and rapidly at 40°C, to give the [4+4] dimer complex **142** via a [3,3] sigmatropic shift (Cope rearrangement) which breaks the C β -C β bridge of complex **141** and forms a new C α' -C α' bond. These series of transformations are summarized in scheme 5.11 and the Cope rearrangement of complex **141** can be seen in scheme 5.12. The X-ray crystal structure of complex **142** can be seen in figure 5.4.

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Scheme 5.11 The P-S-P-linked biphosphole undergoes a [2+2] dimerization followed by a Cope rearrangement to give the [4+4] dimer

Scheme 5.12 The [3,3] sigmatropic shift (Cope rearrangement) of complex **141**.

Figure 5.4 X-ray crystal structure of the [4+4] dimer **142**. Selected distances (Å) and angles (deg.): P1-S1 2.0897(9), S1-P2 2.0857(9), C13-C14 1.570(3), C13-P2 1.859(3), C14-P1 1.866(2), C19-C20 1.580(4), C19-P1 1.855(3), C20-P2 1.863(3), P1-W1 2.4583(6), P2-W2 2.4703(7); P1-S1-P2 87.61(3)°, C14-P1-C19 85.84(11)°, C13-P2-C20 85.97(11)°. Ellipsoids drawn at 50% probability level.

After the final transformation, the P-S bond lengths go back to normal values and the P-S-P angle remains approximately identical at 87.6°. The [4+4] structure **142** proved to be extraordinarily unreactive. All our desulfurization attempts have failed so far.

The question that remains to be solved is why does not complex **140** undergo the symmetry-allowed [4+2] cycloaddition to yield the sulfur analogue of complex **135**, but prefers to give the [2+2] dimer **141** in spite of the strain created at the P-S-P bridge. It has been well established (theoretically and experimentally) that there is a sharp increase in the reactivity of the phosphole dienic system when there is an oxygen substituent at phosphorus (R = OR).^{21,22,23}

Due to the fact that oxygen is highly electronegative, it switches off the hyperconjugation between the diene and the exocyclic P-OR bond.^{21,22,23} This explains why the P-O-P biphosphole **137** is so prone to give the [4+2] dimer. Sulfur which is much less electronegative does not kill the hyperconjugation and thus the P-S-P biphosphole **140** does not undergo the [4+2] cycloaddition. In the P-S-P biphosphole **140** the face-to-face disposition of the two dienes favors the [2+2] cycloaddition. In the [2+2] cycloaddition product **141** the P-S-P bridge is somewhat strained but the weak P-S bond can accommodate this elongation. This would be far more difficult for the stronger P-O bond.

5.3 Conclusion

When the phosphorus lone pair of a phosphole ring is oxidized or complexed it has the tendency to dimerize via a [4+2] cycloaddition. As can be seen by the comparison of the 1-phenyl-3,4-dimethylphosphole oxide **131** and sulfide **133**, the nature of the substitution at phosphorus can affect this dimerization. This report demonstrates that changing P–X–P-linked biphospholes derivatives (X = O, S) from oxygen to sulfur leads to a complete shift from the [4+2] dimerization to the [2+2] dimerization. These findings again highlight the fact that minor changes of the substituent at P can drastically change the reactivity of the phosphole ring.

The preceding work was published in 2011 in the New Journal of Chemistry and was featured as a “Hot Article” on the journal’s website.²⁴

5.4 Experimental

Solvents were dried before use. Silica gel (230-400 mesh) was used for the chromatographic separations. NMR spectra were recorded on either a 400MHz JEOL ECA 400, or JEOL ECA 400SL spectrometer. All spectra were recorded at 298K in CD₂Cl₂ unless otherwise specified. HRMS spectra were obtained on a Water Q-ToF Premier MS. X-ray crystallographic analyses were performed on a Bruker X8 APEX diffractometer. All reactions were performed under argon. All commercially available reagents were used as received from the suppliers.

P-O-P-linked biphosphole tungsten complex (137)

N-methylimidazole (0.04mL, 0.50mmol) was added dropwise at 0°C to a Schlenk containing 1-hydroxy-3,4-dimethylphosphole tungsten complex (0.194g, 0.429mmol) in THF (2mL) under argon. Next 1-chloro-3,4-dimethylphosphole tungsten complex (0.202g, 0.429mmol) dissolved in THF (2mL) was added dropwise at 0°C to the reaction mixture. Next the solvent was removed under vacuum, the crude product was then dissolved in dry methylene chloride and filtered through neutral alumina at 0°C, solvent was then removed under vacuum, to give a orange yellow solid (0.289g, 76% yield).

³¹P NMR (CD₂Cl₂): δ 115.8 ppm (ΣJ_{PW} = 338 Hz); ¹H NMR (CD₂Cl₂): δ 2.09 (d, *J* = 0.9 Hz, 6H, Me), 6.11 (d, ²J_{HP} = 37.6 Hz, 2H, =CH); ¹³C NMR (CD₂Cl₂): δ 17.14 (pseudo-t, ΣJ_{CP} = 12.4 Hz, Me), 127.88 (pseudo-t, ΣJ_{CP} = 42.0 Hz, =CH), 150.53 (pseudo-t, ΣJ_{CP} = 12.4 Hz,

=CMe), 195.94 (pseudo-t, $\Sigma J_{CP} = 7.6$ Hz, *trans*-CO), 199.45 (pseudo-t, $\Sigma J_{CP} = 24.8$ Hz, *cis*-CO).

P-O-P-linked biphosphole tungsten complex [4+2] dimer (135)

N-methylimidazole (0.02mL, 0.25mmol) was added dropwise at 0°C to a Schlenk containing 1-hydroxy-3,4-dimethylphosphole tungsten complex (0.092g, 0.204mmol) in THF (2mL) under argon. Next 1-chloro-3,4-dimethylphosphole tungsten complex (0.102g, 0.216mmol) dissolved in THF (2mL) was added dropwise at 0°C to the reaction mixture. Next the reaction mixture was heated for 3 hours at 40°C. The solvent was then removed under vacuum, and the crude product was purified by column chromatography with a 90:10 hexane: methylene chloride mixture as the eluent ($R_F = 0.33$), solvent was then removed under vacuum, to give a white solid (0.135g, 75% yield). This compound has already been characterized.¹⁹

^{31}P NMR (CD_2Cl_2): δ 139.30 ppm (d, $^2J_{PP} = 24.5$ Hz, $\Sigma J_{PW} = 303$ Hz), 167.62 (d, $^2J_{PP} = 24.4$ Hz, $\Sigma J_{PW} = 302$ Hz); HRMS m/z 886.9287 (calcd for $\text{C}_{22}\text{H}_{17}\text{O}_{11}\text{P}_2^{184}\text{W}_2$, 886.9265).

1-Thiolyl-3,4-dimethylphosphole tungsten complex (139)

Under argon, sulfur (170mg, 5.31mmol) was added at room temperature to a freshly prepared 3,4-dimethylphospholyllithium pentacarbonyltungsten complex solution (5.31 mmol) in THF (20 mL), and allowed to stir for 30 min. The formation of the P-SLi was confirmed by ^{31}P NMR. The solution was then lowered to 0°C and trifluoroacetic acid (0.40mL, 5.31mmol) was added dropwise to the solution, then the solution was allowed to warm up to rt. Next, the solvent was removed under vacuum. The product was purified on silica gel (0°C) using methylene chloride as the eluent, solvent was then removed under vacuum, to give a yellowish-brown solid (1.21 g, 49% yield).

^{31}P NMR (CD_2Cl_2): δ 8.1 ppm ($^1J_{\text{PW}} = 225$ Hz); ^1H NMR (CD_2Cl_2): δ 2.17 (s, 6H, Me), 6.43 (d, 2H, $^2J_{\text{HP}} = 39.8$ Hz, =CH); ^{13}C NMR (CD_2Cl_2): δ 17.23 (d, $^3J_{\text{CP}} = 12.3$ Hz, Me), 132.58 (d, $^1J_{\text{CP}} = 38.1$ Hz, =CH), 150.64 (d, $^2J_{\text{CP}} = 11.1$ Hz, =CMe), 196.13 (d, $^2J_{\text{CP}} = 6.1$ Hz, *trans*-CO), 199.41 (d, $^2J_{\text{CP}} = 22.2$ Hz, *cis*-CO). HRMS m/z 467.9414 (calcd for $\text{C}_{11}\text{H}_9\text{O}_5\text{PS}^{184}\text{W}$, 467.9418).

P-S-P-linked biphosphole tungsten complex (140)

Under argon, sulfur (170mg, 5.31mmol) was added at room temperature to a freshly prepared 3,4-dimethylphospholyllithium pentacarbonyltungsten complex solution

(5.31 mmol) in THF (20 mL), and allowed to stir for 30 min. The formation of the P-SLi (^{31}P δ = 13.6 in THF) was confirmed by ^{31}P NMR. Next 1-chloro-3,4-dimethylphosphole complex (**1**) (2.50 g, 5.31 mmol) was added at room temperature, and stirred for 20 min. The formation of the product was confirmed by ^{31}P NMR. The solvent was removed under vacuum. Next, the product was filtered through silica gel (0°C) using methylene chloride as the eluent. Solvent was then removed under vacuum to give an orange solid (4.26g, 89% yield).

^{31}P NMR (CD_2Cl_2): δ 32.5 ppm ($^1J_{\text{PW}} = 205$ Hz); ^1H NMR (CD_2Cl_2): δ 2.16 (s, 6 H, Me), 6.19 (d, 2H, $^2J_{\text{HP}} = 39.8$ Hz, =CH); ^{13}C NMR (CD_2Cl_2): δ 17.23 (pseudo-t, $\Sigma J_{\text{CP}} = 12.1$ Hz, Me), 128.31 (pseudo-t, $\Sigma J_{\text{CP}} = 38.9$ Hz, =CH), 150.75 (pseudo-t, $\Sigma J_{\text{CP}} = 12.1$ Hz, =CMe), 195.87 (pseudo-t, $\Sigma J_{\text{CP}} = 6.1$ Hz, *trans*-CO), 199.25 (pseudo-t, $\Sigma J_{\text{CP}} = 23.1$ Hz, *cis*-CO). HRMS m/z 902.9014 (calcd for $\text{C}_{22}\text{H}_{17}\text{O}_{10}\text{P}_2\text{S}^{184}\text{W}_2$, 902.9037).

P-S-P-linked biphosphole tungsten complex [2+2] dimer (**141**)

When the P-S-P-linked biphosphole tungsten complex **140** is irradiated with visible light it will form the P-S-P-linked biphosphole tungsten complex [2+2] dimer **141**. Subsequently, it will slowly transform into the P-S-P-linked biphosphole tungsten complex [4+4] dimer **142**. Whenever complex **141** was isolated it, it always contained some of complex **142**.

^{31}P NMR (CD_2Cl_2): δ 96.1 ppm ($^1J_{\text{PW}} = 249$ Hz); ^1H NMR (CD_2Cl_2): δ 1.57 (s, 6H, -C-Me), 1.83 (d, 6H, $J = 1.4$ Hz, =C-Me), 3.68 (pseudo-t, $\Sigma J_{\text{HP}} = 31.1$ Hz, -C-H), 6.00 (d, $^2J_{\text{HP}} = 39.8$

Hz, =C-H); ^{13}C NMR (CD_2Cl_2): δ 18.21 (pseudo-t, $\Sigma J_{\text{CP}} = 12.3$ Hz, -C-Me), 20.47 (pseudo-t, $\Sigma J_{\text{CP}} = 8.6$ Hz, =C-Me), 60.09 (pseudo-q, $\Sigma J_{\text{CP}} = 28.3$ Hz, -C-H), 64.77 (s, -C-Me), 128.13 (d, $^1J_{\text{CP}} = 27.1$ Hz, =C-H), 158.16 (d, $^2J_{\text{CP}} = 7.4$ Hz, =C-Me), 196.43 (pseudo-t, $\Sigma J_{\text{CP}} = 7.3$ Hz, *trans*-CO), 200.58 (pseudo-t, $\Sigma J_{\text{CP}} = 25.8$ Hz, *cis*-CO).

P-S-P-linked biphosphole tungsten complex [4+4] dimer (142)

Under argon, sulfur (170 mg, 5.31 mmol) was added at room temperature to a freshly prepared 3,4-dimethylphospholyllithium pentacarbonyltungsten complex solution (5.31 mmol) in THF (20 mL), and allowed to stir for 30 min. The formation of the P-SLi was confirmed by ^{31}P NMR. Next 1-chloro-3,4-dimethylphosphole complex **70** (2.13 g, 4.53 mmol) was added at room temperature, and stirred for 20 min. The formation of the product was confirmed by ^{31}P NMR. The solvent was removed under vacuum. Next methylene chloride (40mL) was added and the solution was stirred while being irradiated with an 18 W fluorescent (natural light) table lamp for 24 h. The solvent was removed under vacuum and the product was purified by flash chromatography using 3:97 diethyl ether:pentane solution, solvent was then removed under vacuum, to give a white solid (1.75g, 43% yield).

^{31}P NMR (CD_2Cl_2): δ 102.5 ppm ($^1J_{\text{PW}} = 274$ Hz); ^1H NMR (CD_2Cl_2): δ 1.86 (s, 6H, Me), 2.75 (pseudo-t, 2H, $\Sigma J_{\text{HP}} = 5.5$ Hz, CH-P); ^{13}C NMR (CD_2Cl_2): δ 17.14 (pseudo-t, $\Sigma J_{\text{CP}} = 6.1$ Hz, Me), 55.13 (pseudo-t, $\Sigma J_{\text{CP}} = 17.2$ Hz, CH-P), 137.98 (pseudo-t, $\Sigma J_{\text{CP}} = 17.2$ Hz, =CMe), 195.94 (pseudo-t, $\Sigma J_{\text{CP}} = 7.4$ Hz, *trans*-CO), 198.74 (pseudo-t, $\Sigma J_{\text{CP}} = 30.8$ Hz, *cis*-CO). HRMS m/z 902.9035 (calcd for $\text{C}_{22}\text{H}_{17}\text{O}_{10}\text{P}_2\text{S}^{184}\text{W}_2$, 902.9037).

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Chapter 5. Intramolecular [4+2] Versus [2+2] Cycloadditions in P-X-P-Linked
Biphospholes (X = O, S)

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CHAPTER 6

Reaction of Terminal Phosphinidene Complexes with Dihydrogen

6.1 Introduction

The carbene-like chemistry of terminal phosphinidene complexes $[\text{RP-M}(\text{CO})_5]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) has been well established,^{1,2,3,4,5,6} but their reaction with dihydrogen has not been investigated until now. Two recent reports led us to get a closer look at this reaction. The first paper, by Bertrand et. al., described the insertion of reactive singlet carbenes (**143**, **144a,b**) into the H–H bond of dihydrogen (Scheme 6.1).⁷ This was very intriguing because it had been known for some time that cyclic di(amino)carbenes (N-heterocyclic carbenes or NHCs) do not react with dihydrogen.⁸ It should be stressed that terminal phosphinidene complexes $[\text{RP-M}(\text{CO})_5]$ are isolobal with singlet carbenes.

Scheme 6.1 Insertion of reactive singlet carbenes into the H–H bond of dihydrogen

The second paper, by Ruiz et. al., described the reaction of a very bulky bridging η^2 -phosphinidene complex **145** with H_2 , which led to a primary phosphine η^1 complex **146** with the breaking of one P–M bond.⁹ Interestingly enough, complex **146**, synthesized by

another route, is the necessary precursor to generate the bridging η^2 -phosphinidene complex **145** to begin with.⁹

Scheme 6.2 Reaction of a bulky bridging η^2 -phosphinidene complex with H_2

We were curious to see whether it would be possible to duplicate these reactions with terminal phosphinidene complexes $[\text{RP-M}(\text{CO})_5]$. To some degree, the answer is positive, although the reaction conditions are harsher and the mechanism of the reaction is quite different.

6.2 Results and discussion

Our initial experiments were performed with $[\text{PhP-W}(\text{CO})_5]$, generated from its corresponding 7-phosphanorbornadiene precursor **6**. The 7-phosphanorbornadiene tungsten complex **6** was heated in an autoclave with hydrogen at variable temperature and pressure. At 150°C under 20 bar of H_2 there was a complete conversion (i.e. no other products visible by ^{31}P NMR) into the expected phenylphosphine tungsten complex **148** (Scheme 6.3). As can be seen, these conditions are significantly harsher than those used with carbenes and bridging phosphinidenes, where the reaction takes place between 25 - 35°C . However, it must be stressed, that the 7-phosphanorbornadiene precursor **6** yields the terminal phosphinidene complex **147** only above 100 - 110°C .

Scheme 6.3 Reaction of a phenylphosphinidene tungsten complex with dihydrogen at 150°C

In order to have some insight into the possible mechanism, we repeated the experiment at 120°C, and obtained some unexpected results (Scheme 6.4). The trace product **150** has already been described and comes from the addition of trace amounts of water to the terminal phosphinidene complex **147**.¹⁰ The major product **149a,b** is formed as a mixture of two diastereomers. The structure of the *rac* isomer was fully established by X-ray crystal structure analysis (Figure 6.1).

Scheme 6.4 Reaction of a phenylphosphinidene tungsten complex with dihydrogen at 120°C

Figure 6.1 X-ray crystal structure of *rac*-diphosphine complex **149**. Selected bond lengths (Å) and angles (deg.): W1–P1 2.4931(9), W2–P2 2.4961(9), P1–C6 1.820(4), P2–C12 1.817(4), P1–P2 2.2352(13); P2–P1–W1 119.04(4)°, P2–P1–H 97(2)°, P2–P1–C6 105.38(12)°, W1–P1–P2–W2 166.77°, C6–P1–P2–C12 78.23°, H–P1–P2–H 82.3°. Ellipsoids drawn at 50% probability level.

When **149a,b** is heated at 150°C under 20 bar of H₂, it is completely transformed (i.e. no other compounds visible by ³¹P NMR) into complex **148** (Scheme 6.5). Thus **149a,b** appears to be the initial product of the reaction of hydrogen and phenylphosphinidene complex **147**.

Scheme 6.5 Reaction of diphosphine complex **149a,b** with hydrogen at 150°C

An obvious explanation for the formation of complex **149** would be the dimerization of the terminal phosphinidene complex **147** to give the diphosphene **151**, followed by the addition of H₂ onto the P=P double bond (Scheme 6.6). We have indeed demonstrated that the last step can cleanly proceed at 90°C under 20 bar of H₂ for 16 hours (Scheme 6.7). However, this pathway is unlikely, because the dimerization of the terminal phosphinidene **147** does not take place without the presence of copper chloride.¹¹

Scheme 6.6 One pathway for explaining the formation of diphosphine **149**

Scheme 6.7 The reaction of diphosphene **151** with hydrogen to give diphosphine **149**

Another possibility (as suggested by one of the reviewers) would be the insertion of the terminal phosphinidene **147** into the P–H bond of complex **148**. In order to check this possibility, we generated the terminal phosphinidene **147** in the presence of complex **148** at 120°C in toluene and in the absence of H₂ and only traces of **149a,b** were observed. These observations lead us to propose the following mechanism for the reaction of the phenylphosphinidene complex **147** with H₂ (Scheme 6.8).

Scheme 6.8 Proposed mechanism for the reaction of [PhP-W(CO)₅] with H₂

This mechanism is closely related to the well-known conversion of [H-Co(CO)₄] into [Co₂(CO)₈] via the intermediate radical [Co(CO)₄][•] formed by homolysis of the metal-hydrogen bond.¹² To check the likelihood of this mechanism we performed a DFT analysis of complex **152**, at the uB3PW91/6-31G(d)-Lanl2dz(W) level.¹³ The structure is shown in figure 6.2. It corresponds to a local minimum on the energy hypersurface with no negative frequencies.

Figure 6.2 Structure of radical **152** as computed by DFT. Selected bond lengths (Å) and angles (deg.): P1-W23 2.4682, P1-C12 1.7891, P1-H24 1.4138; C12-P1-W23 130.14°, C12-P1-H24 100.84°, H24-P1-W23 122.95.

According to the computed structure of **152**, the P-W bond is relatively short at 2.468 Å, as compared with 2.493 Å for complex **149**, and most likely has some multiple-bond

character. Nevertheless, the phosphorus atom retains some pyramidality ($\Sigma(\text{C-P-C}) = 354^\circ$). The SOMO (Figure 6.3) shows a high localization at phosphorus. According to the calculations, 75% of the spin is localized at P and only 5% at W. This explains why the dimerization takes place at P and supports the proposed mechanism.

Figure 6.3 SOMO (Kohn-Sham) of radical **152**

To be thorough, we decided to react complex **150** with H_2 and made an interesting observation. Complex **150** is converted into the primary phosphine complex **148** at 150°C under 20 bar of H_2 (Scheme 6.9). Many phosphites $\text{P}(\text{OR})_3$ are used as ligands in catalytic reactions in the presence of H_2 , such as the hydroformylation reaction. Their industrial use has been hindered by their sensitivity to hydrolysis. It is interesting to know that hydrogenation of the P–O bond is another possible pathway for their decomposition. The reduction of P–OR to P–H (e.g. in phosphonates $\text{R-P}(\text{O})(\text{OR})_2$, and phosphonites $\text{R-P}(\text{OR})_2$) for the formation of alkyl or aryl substituted primary phosphines has been achieved in the laboratory by using very strong reducing agents, such as LiAlH_4 .¹⁴ Here interestingly, it is being achieved in the presence of hydrogen gas and heat.

Scheme 6.9 The reaction of complex **150** with H₂ to give the primary phosphine complex **148**

Next, we repeated similar experiments with methylphosphinidene complex [MeP-W(CO)₅] **153**, generated from its 7-phosphanorbornadiene precursor complex **154**. The reaction times were slightly longer, but the products were similar. Just above the decomposition temperature of the 7-phosphanorbornadiene precursor **154**, we obtained mainly the diphosphine complex **155a,b** as a mixture of two diastereomers, as well as a minor amount of the methylphosphine complex **156** (Scheme 6.10).

Scheme 6.10 Reaction of a methylphosphinidene tungsten complex with dihydrogen at 120°C

We have been able to crystallize the *meso* isomer of **155**. Its X-ray crystal structure can be seen in figure 6.4. It displays an all-trans conformation. The most striking difference with the structure of *rac*-**149** is the much shorter P–P bond at 2.2061(11) Å in *meso*-**155** vs 2.2352(13) Å for **149**. This most likely reflects the steric repulsion that exists between the two phosphorus subunits in *rac*-**149**.

Figure 6.4 X-ray crystal structure of *meso*-diphosphine complex **155**. Selected bond lengths (Å) and angles (deg.): W1–P1 2.4940(6), P1–C6 1.823(3), P1–P1A 2.2061(11); P1A–P1–W1 119.83(4)°, P1A–P1–H 97.9(15)°, P1A–P1–C6 102.06(9)°, W1–P1–P1A–W1A = C6–P1–P1A–C6A = H–P1–P1A–H = 180.00°. Ellipsoids drawn at 50% probability level.

The primary phosphine complex **156** is the only product (by ^{31}P NMR) when heating in the presence of hydrogen at 150°C for 5 hours (Scheme 6.11).

Scheme 6.11 Reaction of a methylphosphinidene tungsten complex with dihydrogen at 150°C

In their report, Bertrand et. al. have stressed the fact that the reactivity of carbenes toward hydrogen is heavily dependent on the substitution pattern of those carbenes.⁷ We, therefore, decided to check whether the use of an aminophosphinidene

complex such as **158** (Scheme 6.12) would change the course of the reaction with hydrogen.

Scheme 6.12 Generation of the aminophosphinidene complex **158** from its phosphirane complex precursor **157**

In this case, the precursor to the phosphinidene complex is the phosphirane complex **157**,^{15,16} and the phosphinidene is generated at lower temperature ($\sim 70\text{-}90^\circ\text{C}$) as compared to ($\sim 100\text{-}110^\circ\text{C}$) for 7-phosphanorbornadienes. The outcome of the reaction was unexpected. The sole product (by ^{31}P NMR) is the secondary diaminophosphine complex **159** (Scheme 6.13).

Scheme 6.13 The reaction of an aminophosphinidene complex with dihydrogen at 90°C

Complex **159** has been fully characterized by X-ray crystal structure analysis (Figure 6.5). The mechanism of its formation most likely involves the hydrogenolysis of the P–N bond to produce aniline (PhNH_2), which subsequently reacts with the

aminophosphinidene complex **158** to yield complex **159**. On the basis of this result, we can expect a variety of different outcomes depending on the functionalization of the phosphinidene complex, and, in some cases, we might obtain interesting products for further synthetic applications.

Figure 6.5 X-ray crystal structure of the secondary phosphine complex **159**. Selected bond lengths (Å) and angles (deg.): P1–W1 2.4927(5), P1–N1 1.6837(18), P1–N2 1.6710(19); W1–P1–N1 120.08(7)°, W1–P1–N2 112.25(7)°, N1–P1–N2 105.64(10)°. Ellipsoids drawn at 50% probability level.

The preceding work was published in 2012 in Organometallics.¹⁷ The following section includes unpublished results.

Since the reaction of alkyl and aryl phosphinidene complexes with hydrogen succeeded in making the corresponding primary phosphine complexes, we wondered if other substituted phosphinidene complexes could react similarly to generate some difficult-to-make primary phosphine complexes (e.g. H_2PCl , $\text{H}_2\text{PCH}_2\text{Cl}$, H_2POCH_3 metal complexes). First, we attempted to generate the chlorophosphinidene complex, from its

precursor the chlorophosphirane complex **75**,¹⁸ in the presence of dihydrogen, unfortunately only decomposition (i.e. drastic decrease in signal-to-noise ratio) was observed.

Scheme 6.14 Attempt to generate chlorophosphinidene complex with dihydrogen at 80°C

Next we attempted to generate a chloromethylphosphinidene complex, from its precursor complex **160**, in the presence of hydrogen at 120°C, as well as at higher temperatures, only to observe decomposition with formation of a minor amount of the methylphosphine complex **156**. It appears that hydrogenolysis is taking place with addition of dihydrogen across the C–Cl bond in $\text{-PCH}_2\text{Cl}$ to give $\text{-PCH}_3 + \text{HCl}$.

Scheme 6.15 Attempt to generate chloromethylphosphinidene complex with dihydrogen at 120°C

Finally, we attempted to generate a methoxyphosphinidene complex, from its precursor complex **161**,¹⁹ in the presence of hydrogen. Unfortunately the reaction resulted in several products as well as decomposition. Attempts to purify the resulting reaction

mixture were unsuccessful. One of the products in the crude reaction mixture appears to match the ^{31}P NMR data for the known phosphine complex **162**.¹⁹ If this is the case it appears that hydrogenolysis of the P–OMe bond is also taking place.

Scheme 6.16 Attempt to generate methoxyphosphinidene complex with dihydrogen at 110°C

6.3 Conclusion

The reaction of terminal phosphinidene complexes $[\text{RP-W}(\text{CO})_5]$ and hydrogen has been investigated. The reaction conditions are harsher and the mechanism of the reaction is quite different than that of the reaction of carbenes and hydrogen. In this case, we propose a mechanism that involves the addition of dihydrogen across the P–W bond of the terminal phosphinidene complex, followed by homolysis of the newly generated tungsten–hydrogen bond to give an intermediate radical that dimerizes. The intermediate radical is supported by DFT calculations. Further heating at higher temperatures with hydrogen can result in the hydrogenolysis of the P–P bond of the diphosphine to give the primary phosphine complex.

These reactions have proved to be an interesting demonstration of small molecule activation (H_2) with terminal phosphinidene complexes. As is the case with carbenes, the substitution of the phosphinidene complex can result in different reactivities. To better understand the capabilities and limitations of this reaction to form new diphosphine complexes and new primary phosphine complexes, more reactions with different substrates need to be explored.

6.4 Experimental

All reactions were carried out with distilled dry solvents. Silica gel (230-400 mesh) was used for the chromatographic separations. NMR spectra were recorded on either a JEOL ECA 400, or JEOL ECA 400SL spectrometer. All spectra were recorded at 298K. Proton decoupling was applied for ^{13}C and ^{31}P spectra. HRMS were obtained on a Water Q-ToF Premier MS. X-ray crystallographic analyses were performed on a Bruker X8 APEX CCD diffractometer or a Bruker Kappa CCD diffractometer. Purified Hydrogen 99.9995% was used for all reactions. All reactions were performed inside a glass liner in a *Parr Instrument Co.* 4560 Mini Bench Top Reactor, using a *Parr Instrument Co.* 4848 Reactor Controller.

Phenylphosphine tungsten complex (**148**)

Reaction of dihydrogen with [PhP-W(CO)₅] at 150°C

To the *Parr* reactor was added 7-phenyl-phosphanorbornadiene tungsten pentacarbonyl complex (0.2006g, 0.31mmol) and toluene (6mL). Next the reactor was filled with hydrogen gas (20.0 bar) and heated for 4 h at 150°C. The reactor was allowed to cool to room temperature, pressure was released, and the reaction mixture was transferred to another flask where the solvent was removed under vacuum. The product was purified by column chromatography (0°C) with 90:10 hexane: methylene chloride solution as the eluent, solvent was then removed under vacuum, to give a white film of complex **148** (0.0383g, 28.8% yield).

^{31}P NMR (CD_2Cl_2): δ -86.2, $^1J_{\text{PW}} = 220$ Hz, $^1J_{\text{PH}} = 343$ Hz (t); ^1H NMR (CD_2Cl_2): δ 5.80 (d, $^1J_{\text{PH}} = 343$ Hz, H-P), 7.47-7.64 (m, Ph); HRMS m/z 433.9539 (calcd for $\text{C}_{11}\text{H}_7\text{O}_5\text{P}^{184}\text{W}$, 433.9541)

Complex **148** has been previously described.²⁰

*Reaction of dihydrogen with **149a,b** at 150°C*

To the *Parr* reactor was added the two inseparable isomers of diphosphine **149** (0.0418g, 0.048mmol) and toluene (6mL). Next the reactor was filled with hydrogen gas (20.0 bar) and heated for 3 h at 150°C. The reactor was allowed to cool to room temperature, pressure was released, and the reaction mixture was transferred to another flask where the solvent was removed under vacuum. The product was purified by column chromatography (0°C) with 90:10 hexane: methylene chloride solution as the eluent, solvent was then removed under vacuum, to give a white film of complex **148** (0.0227g, 54.2% yield).

*Reaction of dihydrogen with **150** at 150°C*

To the *Parr* reactor was added complex **150** (0.1116g, 0.25mmol) and toluene (6mL). Next the reactor was filled with hydrogen gas (20.0 bar) and heated for 10 h at 150°C. The reactor was allowed to cool to room temperature, pressure was released, and the reaction mixture was transferred to another flask where the solvent was removed under vacuum. The product was purified by column chromatography (-5°C) with 90:10 hexane: methylene chloride solution as the eluent, solvent was then removed under vacuum, to give a white film of complex **148** (0.0484g, 45.0% yield).

Diphosphine tungsten complex (149a,b) *Reaction of dihydrogen with [PhP-W(CO)₅] at 120°C*

To the *Parr* reactor was added 7-phenyl-phosphanorbornadiene tungsten pentacarbonyl complex (0.1075g, 0.16mmol) and toluene (6mL). Next the reactor was filled with hydrogen gas (20.0 bar) and heated for 3 h at 120°C. The reactor was allowed to cool to room temperature, pressure was released, and the reaction mixture was transferred to another flask where the solvent was removed under vacuum. The product was purified by column chromatography (0°C) with 90:10 hexane: methylene chloride solution as the eluent, solvent was then removed under vacuum, to give a colorless film containing two inseparable isomers (0.0223g, 31.3% yield). Crystals were grown from a 50:50 hexane: methylene chloride solution at -25°C.

Isomer A:

³¹P NMR (CD₂Cl₂): δ -19.7, ¹J_{PH} = 345 Hz, ΣJ_{PW} = 152 Hz; ¹H NMR (CD₂Cl₂): δ 6.40 (d, ¹J_{PH} = 345 Hz, H-P), 7.33-7.58 (m, Ph); ¹³C NMR (CD₂Cl₂): δ 130.24 (pseudo-t, ΣJ_{CP} = 3.8 Hz, *meta* C), 130.60 (pseudo-t, ΣJ_{CP} = 18.1 Hz, *ipso* C), 132.44 (s, *para* C), 133.71 (pseudo-t, ΣJ_{CP} = 6.7 Hz, *ortho* C), 195.64 (s, *cis* CO), 198.12 (pseudo-t, ΣJ_{CP} = 12.4 Hz, *trans* CO); HRMS *m/z* 866.8997 (calcd for C₂₂H₁₃O₁₀P₂¹⁸⁴W₂, 866.9003)

Isomer B:

³¹P NMR (CD₂Cl₂): δ -22.8, ¹J_{PH} = 352 Hz, ΣJ_{PW} = 161 Hz; ¹H NMR (CD₂Cl₂): δ 6.41 (d, ¹J_{PH} = 352 Hz, H-P), 7.33-7.58 (m, Ph); ¹³C NMR (CD₂Cl₂): δ 128.78 (pseudo-t, ΣJ_{CP} = 18.1 Hz, *ipso* C), 129.90 (pseudo-t, ΣJ_{CP} = 3.8 Hz, *meta* C), 132.19 (s, *para* C), 134.38 (pseudo-t, ΣJ_{CP} = 6.7 Hz, *ortho* C), 195.89 (s, *cis* CO), 198.33 (pseudo-t, ΣJ_{CP} = 12.4 Hz, *trans* CO); HRMS *m/z* 866.8997 (calcd for C₂₂H₁₃O₁₀P₂¹⁸⁴W₂, 866.9003)

Diphosphine tungsten complex (155a,b) *Reaction of dihydrogen with [MeP-W(CO)₅] at 120°C*

To the *Parr* reactor was added 7-methyl-phosphanorbornadiene tungsten pentacarbonyl complex (0.1994g, 0.34mmol) and toluene (7mL). Next the reactor was filled with hydrogen gas (20.0 bar) and heated for 7 h at 120°C. The reactor was allowed to cool to room temperature, pressure was released, and the reaction mixture was transferred to another flask where the solvent was removed under vacuum. The product was purified by column chromatography (-15°C) with 80:20 hexane: methylene chloride solution as the eluent, solvent was then removed under vacuum, to give a light yellow solid containing two inseparable isomers of **155** (0.0273g, 21.9% yield). Crystals were grown from a 50:50 hexane: methylene chloride solution at -25°C.

Isomer A:

³¹P NMR (C₆D₆): δ -62.6, ¹J_{PH} = 342 Hz, ΣJ_{PW} = 156 Hz; ¹H NMR (C₆D₆): δ 1.01 (m, CH₃), 4.12 (dm, H-P); ¹³C NMR (C₆D₆): δ 12.21 (pseudo-t, ΣJ_{CP} = 12.5 Hz, CH₃), 195.76 (pseudo-t, ΣJ_{CP} = 2.9 Hz, *cis* CO), 197.75 (pseudo-t, ΣJ_{CP} = 12.4 Hz, *trans* CO); HRMS *m/z* 742.8691 (calcd for C₁₂H₉O₁₀P₂¹⁸⁴W₂, 742.8690)

Isomer B:

³¹P NMR (C₆D₆): δ -67.0, ¹J_{PH} = 341 Hz, ΣJ_{PW} = 156 Hz; ¹H NMR (C₆D₆): δ 1.01 (m, CH₃), 4.42 (dm, H-P); ¹³C NMR (C₆D₆): δ 10.28 (pseudo-t, ΣJ_{CP} = 14.4 Hz, CH₃), 195.76 (pseudo-t, ΣJ_{CP} = 2.9 Hz, *cis* CO), 197.72 (pseudo-t, ΣJ_{CP} = 12.4 Hz, *trans* CO); HRMS *m/z* 742.8691 (calcd for C₁₂H₉O₁₀P₂¹⁸⁴W₂, 742.8690)

Methylphosphine tungsten complex (156) *Reaction of dihydrogen with [MeP-W(CO)₅] at 150°C*

To the *Parr* reactor was added the 7-methylphosphanorbornadiene tungsten pentacarbonyl complex (0.2286g, 0.39mmol) and toluene (7mL). Next the reactor was filled with hydrogen gas (20.0 bar) and heated for 5 h at 150°C. The reactor was allowed to cool to room temperature, pressure was released, and the reaction mixture was transferred to another flask where the solvent was removed under vacuum. The product was purified by column chromatography (-15°C) with 90:10 hexane: methylene chloride solution as the eluent, solvent was then removed under vacuum, to give a white film of **156** (0.0519g, 36.1% yield).

³¹P NMR (C₆D₆): δ -122.1, ¹J_{PW}= 221 Hz, , ¹J_{PH}= 339 Hz; ¹H NMR (C₆D₆): δ 0.57 (m, CH₃), 3.37 (dq, ¹J_{PH}= 340 Hz, H-P); ¹³C NMR (C₆D₆): δ 4.40 (d, ¹J_{CP}= 31.6 Hz, CH₃), 196.33 (d, ¹J_{CP}= 6.7 Hz, *cis* CO), 199.00 (d, ¹J_{CP}= 21.1 Hz, *trans* CO); HRMS *m/z* 371.9386 (calcd for C₆H₅O₅P¹⁸⁴W, 371.9384)

Complex **156** has been previously described.²¹

Diphenylaminophosphine tungsten complex (159) *Reaction of dihydrogen with [PhNHP-W(CO)₅]*

To the *Parr* reactor was added the 1-phenylaminophosphirane tungsten pentacarbonyl complex¹⁵ (0.1152g, 0.24mmol) and toluene (6mL). Next the reactor was filled with hydrogen gas (20.0 bar) and heated for 4 h at 90°C. The reactor was allowed to cool to room temperature, pressure was released, and the reaction mixture was transferred to another flask where the solvent was removed under vacuum. The product was purified by column chromatography (-10°C) with 70:30 hexane: methylene chloride solution as the eluent, solvent was then removed under vacuum, to give **159** as a faint yellow solid (0.0424g, 64.7% yield). Colorless crystals were grown from a 50:50 hexane: methylene chloride solution at -25°C.

³¹P NMR (CD₂Cl₂): δ 29.8, ¹J_{PW}= 289 Hz, ¹J_{PH}= 401 Hz; ¹H NMR (CD₂Cl₂): δ 5.05 (dd, ²J_{HP}= 14.2 Hz, ³J_{HH}= 6.4 Hz, H-N), 6.98-7.27 (m, H-Ph), 8.02 (dt, ¹J_{HP}= 401 Hz, ³J= 6.4 Hz, H-P); ¹³C NMR (CD₂Cl₂): δ 119.52 (d, ³J_{CP}= 5.7 Hz, *ortho* C), 123.19 (s, *para* C), 129.93 (s, *meta* C) 143.30 (d, ²J_{CP}= 5.8 Hz, *ipso* C) 196.24 (d, ²J_{CP}= 7.7 Hz, *cis* CO), 198.77 (d, ²J_{CP}= 26.9 Hz, *trans* CO); HRMS *m/z* 540.0070 (calcd for C₁₇H₁₃N₂O₅P¹⁸⁴W, 540.0072)

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CHAPTER 7

Insertion of Terminal Phosphinidene Complexes into the Si–H Bond of Silanes

7.1 Introduction

Since their discovery by Mathey,¹ terminal phosphinidenes have been shown to be an extremely powerful tool for making new organophosphorus compounds (see Chapter 1).^{2,3,4} They are known to undergo several types of reactions including: cycloadditions, reactions with nucleophiles, oligomerizations, rearrangements, as well as insertions into σ -bonds. Insertion reaction of phosphinidenes into O–H and N–H bonds,^{1,5} strained C–O and C–N bonds,⁶ carbon–transition metal bonds,⁷ carbon–halogen bonds,⁸ as well as a few isolated examples of insertions into C–H bonds,^{9,10,11} have been described in the literature. Yet the insertion of phosphinidenes into the Si–H bond had not been explored. Thus we began our investigation into the reaction of terminal phosphinidenes with silanes; unfortunately the group of Sterenberg had the same idea in mind and, in 2010, was the first to publish the reaction of their stable cationic electrophilic phosphinidene complex **164** into the Si–H bond of primary, secondary, and tertiary silanes (Scheme 7.1).¹²

Neutral terminal phosphinidene complexes are unstable, transient species, whereas cationic phosphinidene complexes (i.e. with bulky groups on phosphorus and bulky ligands on the metal), generated by chloride abstraction from chloro-phosphido ligands (such as complex **163**), are thermally stable and isolable. As mentioned in chapter one, cationic electrophilic phosphinidenes combine the use of electron-donating (i.e. Cp, Cp*, PPh₃) and electron-withdrawing (i.e. CO) ligands, and contain a bulky diisopropylamino substituent that acts as a π -donor to the electron-deficient

phosphorus atom to help stabilize the singlet state, but it is ultimately the cationic charge that enhances the electrophilicity of these species. The inherent stability of cationic electrophilic phosphinidenes (such as complex **164**) allow the possibility of carrying out reactions at room temperature or lower, but their electron-donating ligands, bulky amino group, and cationic charge can also lead to a decreased and sometimes different reactivity compared to their neutral electrophilic terminal phosphinidene analogues.

Scheme 7.1 Sterenberg et. al. work of trapping of a cationic phosphinidene complex into primary, secondary, and tertiary silanes

An example of this decreased reactivity can be seen in that fact that stable cationic electrophilic phosphinidenes are not electrophilic enough to activate C–H bonds directly, and this, in turn, was the reason Sterenberg et. al. searched for weaker X–H bonds to activate and eventually focused on the Si–H bond.¹²

Sterenberget al. were able to isolate and characterize complexes **165**, **166**, and **167** and were able to obtain an X-ray crystal structure of complex **166**. Unfortunately their attempts to explore the chemistry of the silyl phosphine complexes **165**, **166**, **167** was in the most part unsuccessful due to the fact that the silyl phosphine complexes are extremely sensitive to P–Si bond cleavage. Most of their attempted reactions led to loss of the silyl group and formation of the bridging phosphido complex **168**. Complex **168** was also observed during attempts to crystallize the silyl phosphine complexes, most likely as a result of reactions with traces of water. Formation of complex **168** also occurs in high yields by reacting complexes **165**, **166**, **167** with phenol.

Scheme 7.2 The secondary silyl amino phosphine complexes all resulted in loss of the silyl group and formation of the bridging phosphido complex **168**

The proposed mechanism, by Sterenberg et. al., for the formation of complex **168** can be seen in Scheme 7.3. It begins with nucleophilic attack by phenol at silicon, breaking the P–Si bond. The neutral iron phosphido complex **169** is then protonated to form the primary aminophosphine complex **170**. The side product **171** was identified by GC-MS. Support for the intermediacy of **170** comes from its observation as a fragment in the electrospray mass spectra. Direct experimental evidence for the known unstable side product **172** was not observed, which they believe was due to its decomposition. In a later publication Sterenberg et. al. also showed the ability of a transient cationic alkyl phosphinidene complex to insert into the Si–H bond of a secondary silane.¹³ The

following is some of our preliminary results describing the insertion of terminal phosphinidenes into the Si-H bonds of silanes.

Scheme 7.3 Sterenberg et. al. proposed mechanism for the formation of the bridging phosphido complex **168**

7.2 Results and Discussion

We first decided to explore the reaction of the simplest terminal phosphinidene complex, the phenylphosphinidene complex **147**,¹ generated from the known 7-phenyl-7-phosphanorbornadiene complex **6**.¹⁴ As we generated the phenylphosphinidene complex **147** in the presence of phenylsilane we observed two peaks forming by ³¹P NMR (Scheme 7.4). The first was a peak at $\delta = -110.9$, $^1J_{PW} = 201$ Hz, $^1J_{PH} = 326$ Hz (doublet). The ³¹P-¹H coupling of 326 Hz is a large coupling indicating a proton directly bonded to phosphorus, and the doublet indicates the presence of a single hydrogen atom coupled and directly bonded to the phosphorus, thus supporting the product **173** as the insertion of the phenylphosphinidene **147** into the Si-H bond of phenylsilane. Another peak that also began to grow as the reaction progressed was at $\delta = -89.0$, $^1J_{PW} = 230$ Hz, $^1J_{PH} = 344$ Hz (triplet). The ³¹P-¹H coupling of 344 Hz is a large coupling indicating a proton(s) directly bonded to phosphorus, and the triplet indicates the

presence of two hydrogen atoms coupled and directly bonded to the phosphorus. Once the starting material had been consumed any complex **173** remaining that was exposed to moisture was converted into the final complex **148**. Sterenberg et. al. have stressed the fact that the P–Si bond is extremely sensitive to cleavage for example even by traces of water.¹² Unlike their case, in which the final product is the bridging phosphido complex **168**, our final product after P–Si bond cleavage is the primary phosphine complex. Thus insertion of terminal phosphinidenes into the Si–H bond of silanes and then allowing the P–Si bond to cleave through exposure of moisture, or reaction with alcohols, results in the formation of primary phosphine complexes.

Scheme 7.4 Trapping reaction of phenylphosphinidene complex with phenylsilane

Next we decided to try trapping a methoxyphosphinidene complex with phenylsilane to see if we could get the primary methoxyphosphine complex **177** as well. When the methoxyphosphinidene complex **174**, was generated in the presence of phenylsilane, two products were generated, a minor and a major product (**175** and **176**), which had ^{31}P signals at $\delta = 67.2$ and -210.5 , respectively. Upon exposure to moisture the P–Si bonds were cleaved and resulted in the formation of the minor product **177** and the major product **178**. From the ^{31}P NMR data we could see that the insertion of the methoxyphosphinidene complex **174** into the Si–H bond of phenylsilane was successful, however, it appeared that the phenylsilane was also able to remove off the methoxy substituent as well, to create the parent phosphine complex **178** as the major product.

Scheme 7.5 Trapping reaction of methoxyphosphinidene complex with phenylsilane

From our experiments we had realized that the reducing power of the phenylsilane was too strong for certain substituents, such as P–OMe. We believed that if we could increase the steric bulk about the silane, we could slow down the unwanted reaction in which the methoxy group is removed and thus obtain the insertion product of the phosphinidene complex into the Si–H bond as the major product, which after P–Si cleavage would give the primary methoxyphosphine complex **177**.

Next we generated the methoxyphosphinidene complex **174** and successfully trapped it with dimethylphenylsilane to give complex **179** (Scheme 7.6). Complex **179** easily underwent cleavage of the P–Si bond (after exposure to moisture) to give the methoxyphosphine complex **177** ultimately as the final product.

Scheme 7.6 Trapping reaction of methoxyphosphinidene complex with dimethylphenylsilane

Although these results are still preliminary, the implications are very promising. Since we make use of the extremely versatile 7-phosphanorbornadiene approach for the generation of the terminal phosphinidene complex, we have a huge amount of primary phosphine complexes that we may be able to synthesize and use for organophosphorus chemistry.

7.3 Conclusion

Terminal phosphinidenes are able to insert into the Si–H bond of silanes. The newly formed P–Si bond is easily cleaved in the presence of water, or alcohols, to give the primary phosphine complex as the final product. The trapping of terminal phosphinidene complexes with moderately bulky tertiary silanes provides a better compatibility with different substituents on the phosphorus, for the generation of primary phosphine complexes in this manner. Even though the group of Sterenberg was the first to publish the insertion of phosphinidenes into the Si–H bond of silanes, their use of cationic phosphinidene complexes, which only contain bulky amino substituents, limits their scope for this reaction and ultimately results in a different product than its neutral transient terminal phosphinidene counterpart. By using the extremely versatile 7-phosphanorbornadiene approach for the generation of terminal phosphinidene complexes, the kinds of substituents on phosphorus are not limited, which in turn, opens up the possibilities for making hard-to-make primary phosphine complexes for further use in organophosphorus chemistry.

7.4 Experimental

Toluene was dried before use. Silica gel (230-400 mesh) was used for the chromatographic separations. NMR spectra were recorded on either a JEOL ECA 400, or JEOL ECA 400SL spectrometer. All spectra were recorded at 298K in CD₂Cl₂ unless otherwise specified. HRMS spectra were obtained on a Water Q-Tof Premier MS. All reactions were performed under argon. All commercially available reagents were used as received from the suppliers.

Phenylphosphine tungsten complex (**148**)

To a Schlenk under argon was added 7-phenyl-7-phosphanorbornadiene tungsten pentacarbonyl complex **6** (0.040g, 0.0611mmol), toluene (0.6mL), and phenylsilane (0.15mL, 1.22mmol). The reaction was then heated at 110°C for 9.5 hours while monitoring the reaction by ³¹P NMR. Once the starting material had been consumed the reaction was stopped and the reaction mixture was transferred to another flask and the solvent was removed under vacuum. The product was purified by column chromatography (0°C) with 90:10 hexane: methylene chloride solution as the eluent, solvent was then removed under vacuum, to give a white film of complex **148** (0.0098g, 37% yield).

³¹P NMR (CD₂Cl₂): δ -86.2, ¹J_{PW}= 220 Hz, ¹J_{PH}= 343 Hz (t); ¹H NMR (CD₂Cl₂): δ 5.80 (d, ¹J_{PH}= 343 Hz, H-P), 7.47-7.64 (m, Ph); HRMS *m/z* 433.9539 (calcd for C₁₁H₇O₅P¹⁸⁴W, 433.9541)

Complex **148** has been previously described.¹⁵

Methoxyphosphine tungsten complex (177)

To a Schlenk under argon was added 7-methoxy-7-phosphanorbornadiene tungsten pentacarbonyl complex **161** (0.0400g, 0.0658mmol), toluene (0.6mL), and dimethylphenylsilane (0.05mL, 0.326mmol). The reaction was then heated at 90°C for 12.5 hours while monitoring the reaction by ^{31}P NMR. Once the starting material had been consumed the reaction was stopped and the reaction mixture was transferred to another flask and the solvent was removed under vacuum. The product was purified by column chromatography (0°C) with 90:10 hexane: methylene chloride solution as the eluent, solvent was then removed under vacuum, to give a white film of complex **177** (0.0124g, 49% yield).

^{31}P NMR (C_6D_6): δ 57.8, $^1J_{\text{PW}} = 269$ Hz, $^1J_{\text{PH}} = 343$ Hz (t); ^1H NMR (C_6D_6): δ 2.86 (d, $^3J_{\text{PH}} = 12.7$ Hz, Me), 6.22 (d, $^1J_{\text{PH}} = 343$ Hz, P-H).

To date there is only one other reported synthesis of complex **177**.¹⁶

Phosphine tungsten complex (178)

To a Schlenk under argon was added 7-methoxy-7-phosphanorbornadiene tungsten pentacarbonyl complex **161** (0.0404g, 0.0664mmol), toluene (0.5mL), and phenylsilane (0.20mL, 1.33mmol). The reaction was then heated at 110°C for 3.5 hours while monitoring the reaction by ^{31}P NMR. Once the starting material had been consumed the reaction was stopped and the reaction mixture was transferred to another flask and the

solvent was removed under vacuum. The product was purified by column chromatography (0°C) with hexane as the eluent, solvent was then removed under vacuum, to give a white film of complex **178** (0.0158g, 66% yield).

^{31}P NMR (C_6D_6): δ -185.6, $^1J_{\text{PW}} = 211$ Hz, $^1J_{\text{PH}} = 342$ Hz (q)

Complex **178** has been previously described.¹⁷

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APPENDIX

Table A1. Crystal data and structure refinement for compound **70**.

70

Identification code	mat5t	
Empirical formula	C11 H8 Cl O5 P W	
Formula weight	470.44	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.6527(7) Å	$\alpha = 107.800(7)^\circ$.
	b = 10.8920(11) Å	$\beta = 95.428(7)^\circ$.
	c = 11.9177(19) Å	$\gamma = 107.102(5)^\circ$.
Volume	769.55(17) Å ³	
Z	2	
Density (calculated)	2.030 Mg/m ³	
Absorption coefficient	7.792 mm ⁻¹	
F(000)	440	
Crystal size	0.40 x 0.14 x 0.04 mm ³	
Theta range for data collection	3.23 to 28.99°.	
Index ranges	-8<=h<=9, -14<=k<=14, -16<=l<=16	
Reflections collected	17156	
Independent reflections	4047 [R(int) = 0.0255]	
Completeness to theta = 28.99°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.1466	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4047 / 0 / 174	
Goodness-of-fit on F ²	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0167, wR2 = 0.0394	
R indices (all data)	R1 = 0.0210, wR2 = 0.0428	
Largest diff. peak and hole	0.939 and -0.941 e.Å ⁻³	

Appendix: Crystallographic Data

Table A2. Crystal data and structure refinement for compound **72**.

Identification code	mat123r	
Empirical formula	C17 H14 Cl O9 P W	
Formula weight	612.55	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.9029(3) Å	$\alpha = 84.544(2)^\circ$.
	b = 8.9295(4) Å	$\beta = 82.705(2)^\circ$.
	c = 17.0956(8) Å	$\gamma = 66.407(2)^\circ$.
Volume	1095.33(8) Å ³	
Z	2	
Density (calculated)	1.857 Mg/m ³	
Absorption coefficient	5.512 mm ⁻¹	
F(000)	588	
Crystal size	0.40 x 0.40 x 0.30 mm ³	
Theta range for data collection	2.94 to 30.15°.	
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -24 ≤ l ≤ 24	
Reflections collected	32456	
Independent reflections	6414 [R(int) = 0.0455]	
Completeness to theta = 30.15°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.2886 and 0.2165	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6414 / 0 / 266	
Goodness-of-fit on F ²	1.052	
Final R indices [I > 2σ(I)]	R1 = 0.0426, wR2 = 0.1074	
R indices (all data)	R1 = 0.0512, wR2 = 0.1157	
Largest diff. peak and hole	3.941 and -2.527 e.Å ⁻³	

Appendix: Crystallographic Data

Table A3. Crystal data and structure refinement for compound **75**.

75

Identification code	mat7	
Empirical formula	C11 H10 Cl O5 P W	
Formula weight	472.46	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 6.4957(2) Å	$\alpha = 90^\circ$.
	b = 15.7482(5) Å	$\beta = 98.0280(10)^\circ$.
	c = 14.0945(4) Å	$\gamma = 90^\circ$.
Volume	1427.68(8) Å ³	
Z	4	
Density (calculated)	2.198 Mg/m ³	
Absorption coefficient	8.401 mm ⁻¹	
F(000)	888	
Crystal size	0.40 x 0.24 x 0.08 mm ³	
Theta range for data collection	1.95 to 27.50°.	
Index ranges	-8<=h<=8, -20<=k<=20, -18<=l<=18	
Reflections collected	16331	
Independent reflections	3250 [R(int) = 0.0320]	
Completeness to theta = 27.50°	98.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5530 and 0.1340	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3250 / 42 / 172	
Goodness-of-fit on F ²	1.355	
Final R indices [I>2sigma(I)]	R1 = 0.0180, wR2 = 0.0565	
R indices (all data)	R1 = 0.0224, wR2 = 0.0803	
Largest diff. peak and hole	2.149 and -0.920 e.Å ⁻³	

Appendix: Crystallographic Data

Table A4. Crystal data and structure refinement for compound **77**.

77

Identification code	mat55r	
Empirical formula	C ₂₁ H ₁₅ Cl N O ₇ P W	
Formula weight	643.61	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.7825(5) Å b = 9.0683(6) Å c = 17.8781(11) Å	α = 80.100(3)°. β = 82.371(2)°. γ = 66.015(2)°.
Volume	1132.84(13) Å ³	
Z	2	
Density (calculated)	1.887 Mg/m ³	
Absorption coefficient	5.329 mm ⁻¹	
F(000)	620	
Crystal size	0.40 x 0.24 x 0.12 mm ³	
Theta range for data collection	2.87 to 35.50°.	
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -29 ≤ l ≤ 28	
Reflections collected	51981	
Independent reflections	10307 [R(int) = 0.0258]	
Completeness to theta = 35.50°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5672 and 0.2244	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	10307 / 0 / 291	
Goodness-of-fit on F ²	1.062	
Final R indices [I > 2σ(I)]	R1 = 0.0148, wR2 = 0.0333	
R indices (all data)	R1 = 0.0165, wR2 = 0.0339	
Largest diff. peak and hole	0.776 and -0.966 e.Å ⁻³	

Appendix: Crystallographic Data

Table A5. Crystal data and structure refinement for compound **92**.

Identification code	mat66	
Empirical formula	C ₂₆ H ₂₁ O ₆ P W	
Formula weight	644.25	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 12.6270(4) Å b = 10.9006(3) Å c = 18.1677(6) Å	α = 90°. β = 105.951(2)°. γ = 90°.
Volume	2404.35(13) Å ³	
Z	4	
Density (calculated)	1.780 Mg/m ³	
Absorption coefficient	4.911 mm ⁻¹	
F(000)	1256	
Crystal size	0.40 x 0.40 x 0.30 mm ³	
Theta range for data collection	2.57 to 33.00°.	
Index ranges	-19 ≤ h ≤ 19, -16 ≤ k ≤ 16, -27 ≤ l ≤ 27	
Reflections collected	41283	
Independent reflections	9059 [R(int) = 0.0362]	
Completeness to theta = 33.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.3205 and 0.2441	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9059 / 0 / 309	
Goodness-of-fit on F ²	1.020	
Final R indices [I > 2σ(I)]	R1 = 0.0212, wR2 = 0.0449	
R indices (all data)	R1 = 0.0277, wR2 = 0.0471	
Largest diff. peak and hole	2.767 and -1.147 e.Å ⁻³	

Appendix: Crystallographic Data

Table A6. Crystal data and structure refinement for compound **93**.

93

Identification code	mat68s	
Empirical formula	C ₃₀ H ₁₈ N O ₈ P W	
Formula weight	735.27	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.2300(2) Å	α = 98.9660(10)°.
	b = 10.4232(2) Å	β = 96.9330(10)°.
	c = 18.6007(4) Å	γ = 93.6230(10)°.
Volume	1369.68(5) Å ³	
Z	2	
Density (calculated)	1.783 Mg/m ³	
Absorption coefficient	4.329 mm ⁻¹	
F(000)	716	
Crystal size	0.40 x 0.20 x 0.12 mm ³	
Theta range for data collection	1.98 to 26.04°.	
Index ranges	-6 ≤ h ≤ 8, -12 ≤ k ≤ 12, -22 ≤ l ≤ 22	
Reflections collected	14377	
Independent reflections	5318 [R(int) = 0.0215]	
Completeness to theta = 26.04°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6246 and 0.2763	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5318 / 0 / 370	
Goodness-of-fit on F ²	1.111	
Final R indices [I > 2σ(I)]	R ₁ = 0.0196, wR ₂ = 0.0419	
R indices (all data)	R ₁ = 0.0215, wR ₂ = 0.0425	
Largest diff. peak and hole	1.155 and -0.825 e.Å ⁻³	

Appendix: Crystallographic Data

Table A7. Crystal data and structure refinement for compound **97**.

97

Identification code	mat70r	
Empirical formula	C ₂₂ H ₂₃ Cl ₂ O P S	
Formula weight	437.33	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.3935(4) Å	α = 91.016(2)°.
	b = 10.3039(4) Å	β = 92.609(2)°.
	c = 12.5565(5) Å	γ = 103.638(2)°.
Volume	1053.79(8) Å ³	
Z	2	
Density (calculated)	1.378 Mg/m ³	
Absorption coefficient	0.493 mm ⁻¹	
F(000)	456	
Crystal size	0.40 x 0.36 x 0.14 mm ³	
Theta range for data collection	1.62 to 33.00°.	
Index ranges	-12<=h<=12, -15<=k<=15, -14<=l<=19	
Reflections collected	35974	
Independent reflections	7910 [R(int) = 0.0290]	
Completeness to theta = 33.00°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9342 and 0.8272	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7910 / 0 / 246	
Goodness-of-fit on F ²	1.090	
Final R indices [I>2sigma(I)]	R1 = 0.0365, wR2 = 0.0973	
R indices (all data)	R1 = 0.0464, wR2 = 0.1101	
Largest diff. peak and hole	0.583 and -0.487 e.Å ⁻³	

Appendix: Crystallographic Data

Table A8. Crystal data and structure refinement for compound **122**.

122

Identification code	mat17	
Empirical formula	C11 H9 O6 P W	
Formula weight	452.00	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 8.7113(2) Å	$\alpha = 90^\circ$.
	b = 13.5899(3) Å	$\beta = 90^\circ$.
	c = 23.3608(5) Å	$\gamma = 90^\circ$.
Volume	2765.58(11) Å ³	
Z	8	
Density (calculated)	2.171 Mg/m ³	
Absorption coefficient	8.486 mm ⁻¹	
F(000)	1696	
Crystal size	0.28 x 0.24 x 0.20 mm ³	
Theta range for data collection	1.73 to 26.00°.	
Index ranges	-10 ≤ h ≤ 10, -12 ≤ k ≤ 16, -28 ≤ l ≤ 28	
Reflections collected	23244	
Independent reflections	5405 [R(int) = 0.0367]	
Completeness to theta = 26.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.2816 and 0.1997	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5405 / 0 / 349	
Goodness-of-fit on F ²	1.102	
Final R indices [I > 2sigma(I)]	R1 = 0.0238, wR2 = 0.0574	
R indices (all data)	R1 = 0.0249, wR2 = 0.0587	
Largest diff. peak and hole	1.106 and -2.807 e.Å ⁻³	

Appendix: Crystallographic Data

Table A9. Crystal data and structure refinement for compound **123**.

Identification code	mat25s	
Empirical formula	C ₁₇ H ₁₅ O ₁₀ P W	
Formula weight	594.11	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.68670(10) Å	α = 90.1590(10)°.
	b = 10.5452(2) Å	β = 93.8690(10)°.
	c = 12.8092(2) Å	γ = 100.3990(10)°.
Volume	1018.79(3) Å ³	
Z	2	
Density (calculated)	1.937 Mg/m ³	
Absorption coefficient	5.799 mm ⁻¹	
F(000)	572	
Crystal size	0.36 x 0.34 x 0.08 mm ³	
Theta range for data collection	3.04 to 45.50°.	
Index ranges	-7 ≤ h ≤ 15, -21 ≤ k ≤ 21, -25 ≤ l ≤ 25	
Reflections collected	91270	
Independent reflections	17219 [R(int) = 0.0342]	
Completeness to theta = 45.50°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6541 and 0.2293	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	17219 / 0 / 266	
Goodness-of-fit on F ²	1.040	
Final R indices [I > 2σ(I)]	R1 = 0.0196, wR2 = 0.0416	
R indices (all data)	R1 = 0.0256, wR2 = 0.0436	
Largest diff. peak and hole	1.343 and -1.490 e.Å ⁻³	

Appendix: Crystallographic Data

Table A10. Crystal data and structure refinement for compound **139**.

139

Identification code	mat62s	
Empirical formula	C11 H9 O5 P S W	
Formula weight	468.06	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 6.3749(2) Å	$\alpha = 90^\circ$.
	b = 20.3759(6) Å	$\beta = 112.8780(10)^\circ$.
	c = 12.1540(3) Å	$\gamma = 90^\circ$.
Volume	1454.54(7) Å ³	
Z	4	
Density (calculated)	2.137 Mg/m ³	
Absorption coefficient	8.205 mm ⁻¹	
F(000)	880	
Crystal size	0.40 x 0.40 x 0.30 mm ³	
Theta range for data collection	2.00 to 37.00°.	
Index ranges	-10<=h<=10, -34<=k<=34, -20<=l<=20	
Reflections collected	32910	
Independent reflections	7391 [R(int) = 0.0441]	
Completeness to theta = 37.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.1922 and 0.1379	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7391 / 1 / 177	
Goodness-of-fit on F ²	1.150	
Final R indices [I>2sigma(I)]	R1 = 0.0285, wR2 = 0.0630	
R indices (all data)	R1 = 0.0344, wR2 = 0.0653	
Largest diff. peak and hole	2.313 and -3.421 e.Å ⁻³	

Appendix: Crystallographic Data

Table A11. Crystal data and structure refinement for compound **140** and **141**.

Identification code	mat51r	
Empirical formula	C22 H16 O10 P2 S W2	
Formula weight	902.05	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 20.3643(8) Å	$\alpha = 90^\circ$.
	b = 6.6200(3) Å	$\beta = 97.883(2)^\circ$.
	c = 20.5323(8) Å	$\gamma = 90^\circ$.
Volume	2741.8(2) Å ³	
Z	4	
Density (calculated)	2.185 Mg/m ³	
Absorption coefficient	8.628 mm ⁻¹	
F(000)	1688	
Crystal size	0.32 x 0.26 x 0.20 mm ³	
Theta range for data collection	2.00 to 35.00°.	
Index ranges	-32<=h<=31, -10<=k<=10, -33<=l<=33	
Reflections collected	45737	
Independent reflections	12043 [R(int) = 0.0772]	
Completeness to theta = 35.00°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.2772 and 0.1689	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	12043 / 287 / 460	
Goodness-of-fit on F ²	1.093	
Final R indices [I>2sigma(I)]	R1 = 0.0442, wR2 = 0.1049	
R indices (all data)	R1 = 0.0586, wR2 = 0.1188	
Largest diff. peak and hole	4.363 and -3.833 e.Å ⁻³	

Appendix: Crystallographic Data

Table A12. Crystal data and structure refinement for compound **142**.

Identification code	mat54s	
Empirical formula	C22 H16 O10 P2 S W2	
Formula weight	902.05	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.34540(10) Å	$\alpha = 97.99^\circ$.
	b = 9.55690(10) Å	$\beta = 98.7280(10)^\circ$.
	c = 17.2960(2) Å	$\gamma = 98.47^\circ$.
Volume	1330.12(3) Å ³	
Z	2	
Density (calculated)	2.252 Mg/m ³	
Absorption coefficient	8.892 mm ⁻¹	
F(000)	844	
Crystal size	0.40 x 0.16 x 0.12 mm ³	
Theta range for data collection	2.58 to 31.08°.	
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -25 ≤ l ≤ 23	
Reflections collected	22739	
Independent reflections	8467 [R(int) = 0.0313]	
Completeness to theta = 31.08°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4150 and 0.1251	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8467 / 0 / 338	
Goodness-of-fit on F ²	1.054	
Final R indices [I > 2σ(I)]	R1 = 0.0209, wR2 = 0.0472	
R indices (all data)	R1 = 0.0252, wR2 = 0.0488	
Largest diff. peak and hole	1.209 and -1.433 e.Å ⁻³	

Appendix: Crystallographic Data

Table A13. Crystal data and structure refinement for compound **149a,b**.

149a,b

Identification code	mat100	
Empirical formula	C22 H12 O10 P2 W2	
Formula weight	865.96	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.8630(5) Å	α = 90°.
	b = 13.6016(7) Å	β = 93.970(3)°.
	c = 18.8836(10) Å	γ = 90°.
Volume	2527.2(2) Å ³	
Z	4	
Density (calculated)	2.276 Mg/m ³	
Absorption coefficient	9.276 mm ⁻¹	
F(000)	1608	
Crystal size	0.40 x 0.12 x 0.10 mm ³	
Theta range for data collection	2.07 to 30.55°.	
Index ranges	-14 ≤ h ≤ 14, -12 ≤ k ≤ 19, -27 ≤ l ≤ 27	
Reflections collected	34225	
Independent reflections	7712 [R(int) = 0.0344]	
Completeness to theta = 30.55°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4573 and 0.1189	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7712 / 1 / 331	
Goodness-of-fit on F ²	1.070	
Final R indices [I > 2σ(I)]	R1 = 0.0235, wR2 = 0.0506	
R indices (all data)	R1 = 0.0296, wR2 = 0.0583	
Largest diff. peak and hole	2.581 and -1.373 e.Å ⁻³	

Appendix: Crystallographic Data

Table A14. Crystal data and structure refinement for compound **155a,b**.

155a,b

Identification code	mat117s	
Empirical formula	C ₁₂ H ₈ O ₁₀ P ₂ W ₂	
Formula weight	741.82	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.6181(2) Å b = 8.0445(2) Å c = 9.5458(2) Å	α = 83.8890(10)°. β = 75.2740(10)°. γ = 75.0410(10)°.
Volume	474.41(2) Å ³	
Z	1	
Density (calculated)	2.597 Mg/m ³	
Absorption coefficient	12.329 mm ⁻¹	
F(000)	338	
Crystal size	0.08 x 0.08 x 0.04 mm ³	
Theta range for data collection	2.21 to 31.00°.	
Index ranges	-9 ≤ h ≤ 9, -11 ≤ k ≤ 11, -13 ≤ l ≤ 13	
Reflections collected	11299	
Independent reflections	3018 [R(int) = 0.0163]	
Completeness to theta = 31.00°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6383 and 0.4388	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3018 / 0 / 123	
Goodness-of-fit on F ²	1.145	
Final R indices [I > 2σ(I)]	R1 = 0.0127, wR2 = 0.0284	
R indices (all data)	R1 = 0.0134, wR2 = 0.0311	
Largest diff. peak and hole	1.406 and -1.096 e.Å ⁻³	

Appendix: Crystallographic Data

Table A15. Crystal data and structure refinement for compound **159**.

Identification code	mat115s	
Empirical formula	C17 H13 N2 O5 P W	
Formula weight	540.11	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.7581(2) Å	$\alpha = 90^\circ$.
	b = 18.3584(3) Å	$\beta = 105.7250(10)^\circ$.
	c = 10.6825(2) Å	$\gamma = 90^\circ$.
Volume	1842.07(6) Å ³	
Z	4	
Density (calculated)	1.948 Mg/m ³	
Absorption coefficient	6.387 mm ⁻¹	
F(000)	1032	
Crystal size	0.40 x 0.38 x 0.22 mm ³	
Theta range for data collection	2.17 to 38.00°.	
Index ranges	-16 ≤ h ≤ 16, -29 ≤ k ≤ 31, -18 ≤ l ≤ 13	
Reflections collected	37064	
Independent reflections	10025 [R(int) = 0.0279]	
Completeness to theta = 38.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.3339 and 0.1843	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	10025 / 1 / 244	
Goodness-of-fit on F ²	1.174	
Final R indices [I > 2sigma(I)]	R1 = 0.0220, wR2 = 0.0535	
R indices (all data)	R1 = 0.0318, wR2 = 0.0717	
Largest diff. peak and hole	2.149 and -1.713 e.Å ⁻³	

Lewis Base-Stabilized Phosphinidenes

Another possibility for stabilizing the singlet state of phosphinidenes is to donate an electron pair (i.e. a lewis base) into the vacant P_y orbital on phosphorus (Fig. 1.1). Since electron density is donated to the phosphorus it causes these species to be nucleophilic at phosphorus. An example of this Lewis base-stabilized phosphinidene was first demonstrated with phosphines by Burg in 1961 with the synthesis of the unstable compound $\text{Me}_3\text{P} \rightarrow \text{P}-\text{CF}_3$.^{1,2} Two forms can be written for such type of species (**A** and **B**).

Form **A** depicts the structure as a base-stabilized phosphinidene with two lone pairs depicted on the phosphorus. Form **B** can be seen as containing a $\text{P}=\text{P}$ double bond with only a single lone pair on the phosphorus. In 1970, Burg demonstrated that both lone pairs could be complexed by borane to give a much more stable species

$\text{Me}_3\text{P} \rightarrow \text{PCF}_3(\text{BH}_3)_2$ as well as giving support for structure **A**.³

More recently bulky aryl groups (R') were incorporated onto the phosphorus, which allowed for structural identification as well as more detailed investigations into their reactivity.^{4,5} It was found that these compounds react with aldehydes to give phosphalkenes, thus displaying a “phospha-Wittig” reactivity. It has also been shown that these compounds can act as phosphinidene transfer reagents.^{6,7} Mathey et. al. have shown that further complexation of one of the lone pairs on phosphorus of the “phospha-Wittig” reagent with a transition metal complex, such as tungstenpentacarbonyl, can stabilize the organophosphorus precursor as well as the

resulting phosphalkene.^{8,9} As mentioned previously, Cowley has isolated an intramolecular amine-coordinated amidophosphinidene complex (Scheme 1.19).¹⁰

Another Lewis base that has been incorporated to stabilize phosphinidenes are carbenes. Both acyclic diaminocarbenes¹¹ and N-heterocyclic carbenes (NHC)^{12,13,14,15} have been used. Once again two forms can be written for such type of species (**C** and **D**).

Support for structure **C** was demonstrated in 1997 by Cowley et. al. when they reacted (1,3-dimesityl-imidazolin-2-ylidene)PPh with $\text{BH}_3 \cdot \text{THF}$ to afford the corresponding P-bonded bis(borane) adduct and thus demonstrating the availability of the two lone pairs on phosphorus.¹⁶

When they tried to use BPh_3 as the Lewis acid, it resulted in extrusion of the phenylphosphinidene and formation of cyclopolyphosphines $(\text{PPh})_3$, $(\text{PPh})_4$, and $(\text{PPh})_5$.¹⁶ Mathey et. al. also detected the formation of similar cyclopolyphosphines when they generated an *N*-methylimidazole-stabilized phenylphosphinidene complex.¹⁷

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