New aspects of phosphirene chemistry

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NEW ASPECTS OF PHOSPHIRENE CHEMISTRY

DUANGHATHAI PANICHAKUL

School of Physical and Mathematical Sciences

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ABSTRACT

New aspects of phosphirene chemistry

Duanghathai Panichakul

Two methodologies have been tested for the functionalization of phosphirenes. In the first one, the C–Si bond of a 2-silylphosphirene is activated by a substoichiometric quantity of fluoride ion (TBAF) in THF at $-78\text{ }^{\circ}\text{C}$. Using this technique, it is possible to perform a protodesilylation or a functionalization by benzaldehyde. However, at room temperature with a stoichiometry of fluoride, a nucleophilic attack takes place at P, leading to a ring-opened fluorophosphine. Stille cross-coupling with a 2-stannylphosphirene in the presence of $[\text{PdL}_2]$ as a catalyst leads to an alkynylphosphine by [1,3] migration of tin from C to P.

Next, special chemistry of 2-aminophosphirene: the reaction of the bulky ynamine $\text{PhCCN}^t\text{Pr}_2$ with terminal phosphinidene complexes $[\text{R}-\text{PW}(\text{CO})_5]$, generated from phosphanorbornadiene complex, affords the corresponding phosphirenes ($\text{R} = \text{Ph}, \text{OMe}$) and the diphosphetene ($\text{R} = \text{Me}$). The reaction of this phosphirene with dimethyl acetylenedicarboxylate gives the phosphole resulting from the insertion of the alkyne into the P–C(N) bond and the tetrafunctional arene resulting from [2+2+2] cycloaddition of one alkyne with two phosphirene units.

Finally, the reaction of strong Lewis acids with 2-amino-3-phenylphosphirene pentacarbonyltungsten complexes leads to the corresponding 2-amino phosphindoles through the unexpected formation of a bond between phosphorus and one of the *ortho* carbons of the phenyl ring.

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LIST OF SYMBOLS AND ABBREVIATIONS

Alk	Alkyl group
Ar	Aryl group
br	broad
Bu	Butyl group
calcd	calculated
CDCl_3	chloroform- d_1
CD_2Cl_2	methylene chloride- d_2
Cp	cyclopentadienyl
d	doublet (in NMR assignments)
DPPE	1,2-bis(diphenylphosphino)ethane
dd	doublet of doublet (in NMR assignments)
equiv.	equivalent
Et	Ethyl group
g	grams
h	hour(s)

Hex	Hexyl group
HCl	hydrochloric acid
Hz	Hertz
HRMS	high resolution mass spectroscopy
<i>J</i>	coupling constant (in NMR assignments)
<i>i</i> Pr	isopropyl group
m	multiplets (in NMR assignments)
Me	methyl
mg	milligram(s)
min	minute(s)
mmol	millimole(s)
MS	mass spectroscopy
Nu	nucleophile
NMR	Nuclear Magnetic Resonance
OTf	triflate group
Ph	Phenyl
³¹ P NMR	³¹ P{ ¹ H} NMR

ppm	parts per million
q	quartet (in NMR assignments)
s	singlet (in NMR assignments)
sat.	saturated
t	triplet (in NMR assignments)
δ	NMR chemical shift in ppm

CHAPTER 1

Introduction to phosphirene chemistry

1.1 Overview

The chemistry of phosphorus heterocycles is deeply less developed compared with nitrogen, oxygen and sulfur. The discovery of stable phosphirenes **1**, a three-membered phosphorus heterocycle, was first demonstrated in 1982 by Marinetti and Mathey.¹ They were able to isolate the phosphirene derivatives in good yields from the reaction of terminal phosphinidene complexes with alkynes. The structure of phosphirene was proved by X-ray analysis. One year later, Fongers, Hogeveen, and Kingma synthesized 1-chlorophosphirenium salts (**2**) from the reaction of alkynes with phosphorous dichlorides in the presence of aluminum trichloride.² Synthesis of free tervalent 1*H*-phosphirene (**3**) was then reported by Marinetti, Mathey, Fischer, and Mitschler in 1984.³ The obtained free phosphirene shows a highly pyramidal structure which has no overlap between the P lone pair and the C=C bond. The next breakthrough came in 1987 when Wagner, Maas, and Regitz⁴ discovered the first stable 2*H*-phosphirene **4** from the reaction of phosphaaalkyne with diazocyclohexane.

Figure 1.1

Since the report of the first phosphirene demonstrated by Prof. Mathey in 1982, there have been numerous publications describing the structure, physical data, chemical properties, and synthesis of these three-membered phosphorus species. We

shall look more deeply into these phosphirene rings to investigate new approaches and several applications to make more interesting and useful phosphirene compounds.

1.2 Structural data of phosphirenes

Figure 1.2

The structure of phosphiranes **5** (Figure 1.2) shows intracyclic CPC angles that range from 47° to 51° . The lengths of P–C bond are between 1.780 to 1.890 Å and the C–C bond lengths are between 1.460-1.588 Å. This ring is obviously very strained, so it might be very interesting to study the case of the other three-membered phosphorus heterocycles, phosphirenes. Several structural studies containing phosphirenes and their complexes have appeared in the literature since 1982 together with the X-ray analysis. The selected structural data of phosphirene derivatives are shown in Table 1.1.

Table 1.1 The structural data of phosphirene derivatives.

Phosphirenes	Bond angles ($^\circ$)			Bond lengths (Å)		
	C–P–C	C–P–R	P–C–C	P–C	C=C	P–R
6	42.8	106.6 108.6	68.4 68.7	1.787 1.790	1.307	1.831 (P–C)
3	41.8	104.0 104.4	69.1	1.820 1.821	1.299	1.842 (P–C)

Table 1.1 (cont.) The structural data of phosphirene derivatives.

Phosphirenes	Bond angles (°)			Bond lengths (Å)		
	C-P-C	C-P-R	P-C-C	P-C	C=C	P-R
 4	49.2		56.7 74.1	1.634 1.881	1.482	
 7	50.7 (W-P-C)	128.7	44.7 84.6	2.511 1.775	1.954 (W=C)	1.866 (P-C)
 8	44.0	109.4 111.7	67.8 68.3	1.776 1.782	1.332	
 9	46.1		66.9 67.0	1.730 1.732	1.360	1.640 (P-N) 1.799 (P-C)
 10	43.5		68.2	1.750	1.300	1.800 (P-Me)
 11	43.1	107.91 109.11	69.1 67.8	1.789 1.806	1.320	1.820 (P-C)

Table 1.1 (cont.) The structural data of phosphirene derivatives.

Phosphirenes	Bond angles (°)			Bond lengths (Å)		
	C-P-C	C-P-R	P-C-C	P-C	C=C	P-R
 12	43.1		70.9 66.0	1.768 1.828	1.320	1.822 (P-C)
 13	43.2	111.5 113.1	68.8 68.0	1.767 1.757		1.642 (P-O)
 14	44.4	107.09	66.6 68.8	1.752 1.781	1.340	1.680 (P-N)
 15	46.8		66.3 66.9	1.709 1.715	1.360	1.780(P-C) 1.668(P-O) 1.700(P-O)
 16	43.5			1.787	1.320	1.830(P-C)

From Table 1, the C-P-C intracyclic bond angle of phosphirene ranges from 41-49°, compared to phosphiranes (47-51°). The phosphirene shows a range of intracyclic P-C bond and C=C bond lengths in ranges of 1.710-1.880 and 1.300-1.360

Å, respectively. The range of P–C bond of phosphirenes is about the same as in the phosphiranes.

The first X-ray structure of phosphirene complex **6** was reported for the first time by Marinetti, and Mathey in 1982.¹ The structure consists of discrete molecules linked only by Van der Waals and hydrogen bonds. The most interesting point in this structure is related to the P–C1–C2 triangle geometry and it shows the smallest recorded C1–P–C2 bond angle at 42.8°. The P–C intracyclic bond of the ring is surprisingly long (1.790 Å) when compared to the P–R [1.831 (P–C)] bond. Moreover, a C=C bond at 1.307 Å implies that electron density over this phosphirene is poorly delocalized. The structure of uncomplexed phosphirene form **3** was established by X-ray analysis a few years later.³ The intracyclic P–C bonds are about 0.03 Å longer in the uncomplexed ring and become the same as a normal P–C bond. The C–P–C intracyclic bond decreased to 41.8°, whereas the P–C–C intracyclic angles increase by 0.5°. The C=C double bond remains well localized at 1.299 Å. All these data indicate that free phosphirenes have pyramidal character more than the uncomplexed form. In 1987, Wagner, Maas, and Regitz⁴ recorded the X-ray structure of the first phosphorus/carbon three-membered ring containing a P=C double bond **4**. A comparison of structure **4** with the other free⁵ and complexed phosphaaalkenes⁶, the P=C (1.634 Å) is slightly short. Besides, the P–C bond in the phosphirene is about 0.03 Å longer than the normal P–C bond in phosphaaalkene. In the mean time, Tran Huy, Fischer, and Mathey obtained the X-ray crystal structure of a metallaphosphirene **7**.⁵ This structure shows the W–C–P is 50.7°, while the P–C bond length is 1.775 Å which is similar to the P–C bond length in complex **6**. The fifth study on structural data was performed by Nixon et al.⁶ A comparison of phosphirene complex **8** with free triphenylphosphirene **3** indicates three interesting results. Firstly, the intracyclic bond

length between C=C decrease from 1.332 to 1.299 Å. Secondly, The intracyclic bond length of P–C increases from 1.776 to 1.820 Å. Lastly, when phosphirene is complexed to a metal atom, the pyramidalicity at phosphorus decreases. These results indicate that a complexation of phosphirenes gives higher stability to the ring when compared with the free phosphirene due to the suppression of the destabilizing interaction between the lone pair at phosphorus and the double bond. The structure of the phosphirenium salt⁷ **9** shows electronic delocalization within the ring. The C–P–C bond angle is 46.1°, while, the bond lengths between P–C and C=C are 1.730 and 1.360 Å, respectively. Phosphirene **10** gives similar results with the other phosphirenes.⁸ The intracyclic C–P–C bond angle is 43.5 ° and the bond lengths of P–C and C=C are 1.750 and 1.300 Å, respectively. The X-ray crystal structure of phosphirene complex⁹ **11** shows some clue for increasing reactivity when compared to other phosphirene complexes. One of the P–C bond is longer than the other one (1.806 and 1.789 Å). It must be noted that the intracyclic P–C bond lengths of phosphirene complexes **6** and **11** are identical (1.790 and 1.787 Å). The C=C bonds of **11** is longer than **5** (1.320 and 1.307 Å) and implies that the alkynyl substituent in complex **11** weakens the adjacent C=C and P–C bonds, via conjugative stabilizing interaction. In the same vein, phosphirene complex¹⁰ **12** shows the intracyclic C–P–C angle about 43.1° and the bond lengths of C=C bond and P–C bond are 1.320 and 1.768 Å, respectively. Bisphosphirenyl ether complex **13** that consists of two phosphirene units¹¹, gives similar results as phosphirene complex **5**. In 2005, a structure of the first bicyclic phosphirene, 2-aza-1-phospha-bicyclo-[5.1.0]oct-7-ene **14** was confirmed by X-ray analysis¹². The structure of this phosphirene is as expected. The C–P–C angle of 44.4° with normal P–C bond lengths 1.752 and 1.781 Å, and a C=C bond 1.334 Å. The structure of phosphirene complex¹³ **15** shows a very short P–C bonds about 1.709

and 1.715 Å as compared to the corresponding bonds in phosphirene **6** (1.787 and 1.790 Å) as well as the intracyclic C–P–C angle (46.8 Å) and the lengths of C=C (1.360 Å). Recently, a structure of 2,3-dithienyl phosphirene complex¹⁴ **16** was reported by Mathey et. al. The structure shows an intracyclic C–P–C angle of 43.5 ° and P–C bonds of 1.787 and 1.788 Å as well as C=C bond lengths of 1.320 Å.

1.3 Spectroscopic data of phosphirenes

³¹P and ¹³C NMR spectroscopic data of selected phosphirenes are listed in Table 1.2. Free phosphirene **3** shows a large upfield shift of ³¹P NMR resonance at –190.3 ppm and a huge coupling constant of ¹³C NMR (¹J_{CP} = 43.9 Hz).¹ While complexed phosphirenes **6**, **17**, **18** also appear at high field of ³¹P NMR resonance depending on the substituents at phosphorus.^{3,15-16} In the case of phosphirenylium cation **18**, ³¹P resonance appears extremely low field at +309.7 ppm and a large coupling of C–P (¹J_{CP} = 94.9, 83.3 Hz).¹⁷ Phosphirenylium cation with tungsten complex **20** shows ³¹P resonance at +232.6 ppm (¹J_{CP} = 40.5 Hz).¹⁸

Table 1.2 NMR data for some selected phosphirenes.

Phosphirenes	³¹ P	¹³ C
3	–190.3	122.7 (¹ J _{CP} = 43.9 Hz, =C–P)
6	–161.4	130.2 (¹ J _{CP} = 24.0 Hz, =C–P)

Table 1.2 (cont.) NMR data for some selected phosphirenes.

Phosphirenes	^{31}P	^{13}C
 17	-109.7	143.2 ($^1J_{\text{CP}} = 22.0$ Hz, =C-P)
 18	-16.7	149.4 ($^1J_{\text{CP}} = 19.0$ Hz, =C-P)
 19	+309.7	215.4 ($^1J_{\text{CP}} = 94.9$ Hz, =C- <i>t</i> Bu) 197.0 ($^1J_{\text{CP}} = 83.3$ Hz, =C-Ph)
 20	+232.6	197.2 ($^1J_{\text{CP}} = 40.5$ Hz, C=C)

δ , ppm using 85% H_3PO_4 as an external standard

1.4 Aromaticity

Aromaticity has played a crucial role in organic chemistry for over decades and is still a topic for chemists to study more in depth. According to the Hückel rule $[(4n+2)\pi]$, the smallest possible aromatic structure is a three-membered ring that is occupied by 2π electrons. The first to synthesize and characterize the cyclopropenium cation (C_3H_3^+) was Breslow in late 1950.^{19ab} This cation is the smallest 2π Hückel aromatic compound. In the case of a three-membered phosphorus heterocycle, phosphirene derivatives have remained elusive so far. One of the most interesting points in phosphirene chemistry is the aromaticity of phosphirenes. These questions

are far from being solved. Here are some examples of phosphirene derivatives. The structure of phosphirenylium cations **21**, their complexes **22**, and phosphirenium cations **23** could be aromatic species according to the Hückel rule. While phosphirenyl anions **24**, their complexes **25**, and phosphirenium anions **26** could be antiaromatic species.

Figure 1.3

A summary of a few indicators that could be found in the literature concerning aromaticity problems is as follows. In 1985, Deschamps and Mathey²⁰ investigated the synthesis of 1-chlorophosphirenes **17** in the coordination sphere of tungsten by treatment of AlCl_3 with 1- β -chlorophosphirene **27**. They proposed the phosphirenylium cation **29** as an intermediate from the loss of ethylene group in the transient cation **28**, followed by treatment with sat. NH_4Cl to generate **17** (Scheme 1.1).

Scheme 1.1

A few years later, the same authors²¹ demonstrated that bis(phosphirenyl) oxide **30** can give a stable complex at oxygen with AlCl_3 **31**. No phosphirenylium cation **32** and phosphirene oxide anion **33** were observed due to the low stability of this species.

Scheme 1.2

In 1994, Laali and Regitz¹⁷ reported the first successful generation of persistent phosphirenylium cation **19** from the reaction of phosphirene **34** with $\text{B}(\text{OSO}_2\text{CF}_3)_3$ in liquid SO_2 at -78°C under argon. The phosphirenylium cation shows a very characteristic peak of ^{31}P NMR very downfield at $\delta +309.7$ ppm. Due to very low stability, this cation must be kept in liquid SO_2 at below -40°C . It must be noted that

this reaction requires an extremely strong Lewis acid $\text{B}(\text{OSO}_2\text{CF}_3)_3$ to bond with trifluoromethane sulfonate ion leading to $\text{B}(\text{OSO}_2\text{CF}_3)_4^-$.

Scheme 1.3

At the same time, Nixon et al²² described the synthesis and characterization of the first compounds containing a stable η^3 -phosphirenium cation in a red-orange nickel complex **35**. This complex was synthesized by condensation of phosphalkyne ($\text{tBuC}\equiv\text{P}$) with nickel atoms at 77K. The ^{31}P signal of the phosphirenium ring shows relatively high field position at -161.0 ppm.

Scheme 1.4

In 1999, Laali and Regitz¹⁸ demonstrated that the phosphirenium cation can be produced in a coordination sphere of other transition metals such as tungsten. Treatment of phosphirene complex **36** with a strong Lewis acid boron tris(trifluoromethanesulfonate) in liquid SO_2 at -55°C generated phosphirenium complex **20**. The ^{31}P NMR spectra of **20** shows a dramatic shift to $+232.6$ ppm with a huge $J(\text{P-W})$ coupling at 392.8 Hz when compared to starting phosphirene complex δ -35.4 ppm, $J(\text{P-W})$ 343.8 Hz. The large coupling constant of this phosphirenium complex indicates that this phosphirenium cation is coordinated to pentacarbonyl tungsten by η^1 -coordination (Scheme 1.5).

Scheme 1.5

From these results, it is clear that the phosphirenium ion does exist but for an in-depth investigation, the need of a stable species is a prerequisite.

1.5 Reactivity of phosphirenes

Since the discovery of phosphirene in 1982,¹ they have been investigated in-depth for their chemical properties and reactivity. Several papers and reviews have already been written on the reactivity of phosphirenes as shown in the following sections.

1.5.1 Reactions at phosphorus of the ring

Many reports have been described for the type of reaction in which the phosphirene ring remains untouched and we know that the nucleophilicity of the phosphorus lone pair of the ring is very low. It is possible to sulfurize the 1,2,3-triphenylphosphirene (**3**) in the presence of *N*-methylimidazole as a catalyst (Scheme 1.6).^{23a-b}

Scheme 1.6

The reaction of a powerful alkylating agent such as trimethyloxonium tetrafluoroborate with triphenylphosphirene (**3**) in CH_2Cl_2 at room temperature produces a phosphirenium salt **38** (Scheme 1.7).^{23a}

Scheme 1.7

Similarly, bromination of 1,2,3-triphenylphosphirene (**3**) in the presence of AlCl_3 also gives a bromo phosphirenium salt **39** (Scheme 1.8).^{23b}

Scheme 1.8

In 1985, Dechamps and Mathey described another example of a reaction at phosphorus in which a dealkylation is performed by AlCl_3 upon reaction with 1- β -chloroethylphosphirene to give chlorophosphirene **17**. The driving force for this reaction is the aromaticity of **29** (Scheme 1.9).¹⁵

Scheme 1.9

One of the most interesting example is the use of chlorophosphirene complex **17** to generate hydrophosphirene complex **40** by using magnesium and a proton source in THF under ultrasonic irradiation (Scheme 1.10).²¹

Scheme 1.10

Alcoholysis and aminolysis of the P–Cl bond of the chlorophosphirene complex **17** using THF as a solvent afford alkoxyphosphirene **41** and aminophosphirene **42**, respectively. These reactions were performed without ring cleavage (Schemes 1.11 and 1.12).²¹

Scheme 1.11

Scheme 1.12

Hydrophosphirene **40**, as obtained in Scheme 1.10 can be further metalated using *tert*-BuLi affording a complicated complex mixture of unknown products which no longer are phosphirene compounds. Phase transfer technique was then applied for the reaction and it was successful. The addition of the P–H bond of hydrophosphirene complex **40** onto benzaldehyde, acrylonitrile, and dimethyl acetylenedicarboxylate gave good yields of expected products **43–45** (Scheme 1.13).²¹

In the presence of AIBN, cleavage of P–H bond of hydrophosphirene complex **40** induced the breaking of the P–C bond of another molecule of hydrophosphirene complex to give complex **46** (Scheme 1.14).²¹

This reactivity of phosphirene is also extended to nucleophilic substitution reaction of chlorophosphirene **47** with various nucleophiles as shown in Scheme 1.15 to afford a variety of functionalized phosphirenes **48-53**.²⁴

Scheme 1.15

In the presence of $\text{Na}_2\text{Fe(CO)}_4$, free chlorophosphirene **47** can transform to the dimeric structure **54** as shown in Scheme 1.16.²⁵

Scheme 1.16

Another type of interesting point is an oxidative addition of orthoquinone onto halophosphirenes **55** that leads to very stable pentacoordinate phosphirene derivatives **56** (Scheme 1.17).¹⁴

Scheme 1.17

The condensation 1-alkynylphosphirene **57** with terminal phosphinidene unit [PhCCP–W(CO)₅], generated from 1-alkynylphosphanorbornadiene complex, gave biposphirene complex **58**. The next step shows the reaction of biposphirene with the [PhP–W(CO)₅] unit leading to the transformation into a triphosphirene complex **59** (Scheme 1.18).²⁶

Scheme 1.18

1.5.2 Reactions at ring carbon

Only few examples for this type of reaction have been described in the literature. One is the deprotonation at carbon of a phosphirene ring **60** using *n*BuLi, followed by trapping with acetone (Scheme 1.19).²⁷

Scheme 1.19

A second example is the [4+2] cycloaddition at the C=C bond of activated phosphirene **62** with 2,3-dimethyl-1,3-butadiene in toluene leading to phosphirane complex **63** (Scheme 1.20).^{23a}

Scheme 1.20

1.5.3 Reactions with cleavage of one P–C bond of the ring

We shall now take a look at another reactivity of phosphirenes involving the ring cleavage of the P–C bond of the ring. For the first example, hydrolysis of phosphirenium salts **38** leads to the ring-opened product **64** (Scheme 1.21).^{23a}

Scheme 1.21

In the same vein, the hydroxide ion can attack at the phosphorus center of the phosphirene complex to cleave the ring, then protonation to give the hydroxyl complex (Scheme 1.22).^{23a}

Scheme 1.22

It is also possible to cleave the phosphirene complex **6** using UV irradiation with methanol. A mixture of the *Z* and *E* isomers of the ring-opened product is obtained (Scheme 1.23).^{23a}

Scheme 1.23

According to the high electrophilicity of 1,2,3-triphenylphosphirene, it is not surprising that *n*-BuLi can easily attack the phosphorus of this phosphirene to produce the ring-opened anion. This anion can be reacted with methyl iodide followed by sulfurization to afford the two isomeric phosphines **70** and **71** (Scheme 1.24).^{23a}

Scheme 1.24

An alkali metal was also applied to the cleavage of the P–C bond of the ring. The use of naphthalene-sodium radical dianion to react with 1,2,3-triphenylphosphirene **3** to generate dianion intermediate **72**, followed by methylation, protonation, and sulfurization affords the two isomers of the expected products (Scheme 1.25).^{23a}

Scheme 1.25

Following the results mentioned above, it was found that *n*-BuLi not only attacks at the phosphorus center of the phosphirene ring but also deprotonates carbon substituents of the ring. Indeed, deprotonation of phosphirene **75** with *n*-BuLi is followed by ring opening to generate a phosphide anion **77**, which can be treated with electrophiles for example hydrochloric acid, methyl iodide, and trimethylsilyl chloride affording stable allenylphosphine compounds **78** (Scheme 1.26).²⁷

Scheme 1.26

At low temperature metalation of phosphirene **60** with $n\text{-BuLi}$ leads to phosphirene anion **79**. Upon warming the reaction up to room temperature, this intermediate decomposes to give an open chain alkynyl phosphide **80**, which was trapped by methyl iodide to obtain alkynyl phosphine **81** (Scheme 1.27).²⁷

Scheme 1.27

The last example for the cleavage of one P–C bond of the ring is an anionic ring-opening polymerization of the phosphirene. By treatment of phosphirene **82** with 0.1 equiv. of $n\text{-BuLi}$ at $-78\text{ }^\circ\text{C}$ then gradually warming up to room temperature to perform the ring opening, **82** polymerizes to give **83** (Scheme 1.28).²⁸

Scheme 1.28

1.5.4 Reactions with cleavage of two P–C bonds of the ring

Up to now, only few examples of phosphirenes have been described with dissociation of phosphorus and carbon units. Here is the first example, aminophosphirene **43** can be used as a terminal phosphinidene precursor. This transient complex is trapped by 2,3-dimethyl-1,3-butadiene, ethanol, and diethylamine to afford the expected products **84-86** (Scheme 1.29).³⁰

Scheme 1.29

1.5.5 Ring expansions

Expansion of the phosphirene ring can be done with either insertion into the phosphirene units or by internal rearrangements. Selected insertion reactions are described in Scheme 1.30-1.35. Phosphirene metal complexes at $160\text{ }^{\circ}\text{C}$ in the

presence of carbon monoxide pressure can easily insert CO into phosphirene units providing **88** (Scheme 1.30).³¹

Scheme 1.30

Insertion of metal fragments into the strained phosphorus-carbon bond of phosphirene complexes leads to a complex in which phosphorus contains two different metal atoms. This process occurs via 4-membered metallacycle intermediate (Scheme 1.31).³²

Scheme 1.31

Insertion of another phosphorus molecule into the phosphirene unit is also possible affording the diphosphetene compound **92** (Scheme 1.32).³³

Scheme 1.32

In addition, the insertion of alkynes into one of the phosphorus-carbon bonds of phosphirene complex **93** in the presence of $\text{Pd}(\text{PPh}_3)_4$ yields phosphole complexes **94** (Scheme 1.33).³⁴

Scheme 1.33

Also possible is the insertion of terminal phosphinidene units into the conjugatively destabilized P-C2 bond of 2-alkynylphosphirene **95** leads to diphosphetene complex **96** with *cis*-stereochemistry (Scheme 1.34).³⁵

Scheme 1.34

In the same vein, $[\text{PtCl}_2(\text{RNC})_2]$ can insert into the P-C bond of 1,2,3-triphenylphosphirene **3** to give a dimeric insertion product **97** via halogen transfer from Pt to P (Scheme 1.35).³⁶

Scheme 1.35

Scheme 1.36 shows another example for ring expansion of phosphirenes. Under thermal conditions, intramolecular reorganization of 1-allylphosphirenes **98** provides bicyclic phosphiranes **99**.³⁷

Scheme 1.36

In addition to insertion and internal rearrangement, the phosphirene complexes can readily dimerise in the presence of Pd (0) catalyst to give the unexpected head-to-head 1,2-dihydro-1,2-diphosphinine **101** (Scheme 1.37).³⁸

Scheme 1.37

1.6 Synthesis

The general procedure for the syntheses of phosphirenes can be broadly classified into three main groups: from a P and C₂ unit, from a PC and C unit, and from the cyclisation of CPC.

1.6.1 From P and C₂ units

Common methods for the synthesis of phosphirene complexes are generally from terminal phosphinidene complexes **104**. These transient species are synthesized by thermal decomposition of phosphanorbornadiene complexes **103**, generated from cycloaddition of phospholes **102** with dimethyl acetylene dicarboxylate (Scheme 1.38).

Scheme 1.38

More recently, Lammertsma and co-workers reported a new access to phosphinidene complexes from benzophosphepine complexes **107**, generated from homologation-oxidation of commercially available *o*-phthalaldehyde **105** to give 1,2-diethynylbenzene **106** then hydrophosphination with the complexed phosphine yielding benzophosphepine complexes **107** (Scheme 1.39).³⁹

Scheme 1.39

Trapping of the electrophilic terminal phosphinidene complexes **104** with a variety of alkynes yields phosphirene complexes **1**. The resulting phosphirene can be decomplexed by either halogen-tertiary amine methods or displacement with DPPE giving trivalent phosphirenes **3** (Scheme 1.40).^{1,15}

Scheme 1.40

Besides, aminophosphirenes **108** can be synthesized from transient aminophosphinidene complex **86** with alkynes (Scheme 1.41).^{37b}

Scheme 1.41

Due to their phosphinidene-like behaviors, iminophosphanes **109** also react with trapping reagents to give iminophosphirenes **110** (Scheme 1.42).⁴⁰

Scheme 1.42

One of the simplest methods for the synthesis of phosphirenes starts from dichlorophosphines, AlCl_3 , and alkynes at room temperature in dichloromethane to give chlorophosphirenium salts **111**. Reduction of these salts using tributylphosphine affords the expected trivalent phosphirenes **112** (Scheme 1.43).^{41a, b}

Scheme 1.43

Another approach to synthesize phosphirenes from a P and C₂ unit uses titanacyclopropenes **113** and **114**. These complexes react easily with dichlorophosphines to give phosphirenes **112**. This method is useful, especially for the synthesis of 1-chlorophosphirene (Scheme 1.44).⁴²

Scheme 1.44

It was found that not only titanacyclopropenes but also P=O stabilized zirconacyclopropenes **115** can be the starting material for the synthesis of phosphirenes (Scheme 1.45).⁴³

Scheme 1.45

1.6.2 From PC and C units

The next approach to synthesize phosphirene complexes is from PC and C units. This approach requires the availability of phosphalkynes or phosphalkenes with carbene sources. A siloxy-substituted phosphalkene **118** reacts with silyl carbenoid to give an unusual phosphirene **119** (Scheme 1.46).⁴⁴

Scheme 1.46

Similarly, condensation of a stable phosphinocarbene with phosphalkyne yields 2*H*-phosphirene **120** (Scheme 1.47).⁴⁵

Scheme 1.47

Another approach to obtain 1-chlorophosphirenes **121** was via a formal [1,3] chlorine shift from chlorocarbene precursors (Scheme 1.48).^{17, 46}

Scheme 1.48

A similar chemistry has been found later using 1,2-dichlorocyclopropenes **122** (Scheme 1.49).⁴⁷

Scheme 1.49

Finally, the reaction of a chlorocarbene precursor and a silyl-substituted phosphalkene **125** provided chlorophosphirene **121** (Scheme 1.50).⁴⁶

Scheme 1.50

1.6.3 By cyclisation of a C–P–C unit

Only one example was found in the literature for this cyclisation of a C–P–C unit. This approach is controlled by the metallation of a *gem*-dichloro-bis-ylid **127** with *n*-BuLi to afford phosphirenes **129** (Scheme 1.51).^{44, 48}

Scheme 1.51

1.7 References

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CHAPTER 2

New route to functionalized phosphirenes:

Reactivity of 2-silyl- and 2-stannyl-substituted phosphirenes

2.1 Overview

Two methodologies have been tested for the functionalization of phosphirenes. The C–Si bond of a 2-silylphosphirene is activated by a substoichiometric quantity of fluoride ion (TBAF) in THF at $-78\text{ }^{\circ}\text{C}$. Using this technique, it is possible to perform a protodesilylation or a functionalization by benzaldehyde. However, at room temperature with a stoichiometry of fluoride, a nucleophilic attack takes place at P, leading to a ring-opened fluorophosphine. Stille cross-coupling with a 2-stannylphosphirene in the presence of $[\text{PdL}_2]$ as a catalyst leads to an alkynylphosphine by [1,3] migration of tin from C to P.

Panichakul, D.; Lim, Y.-W.; Mathey, F. *Organometallics* **2010**, 29, 1985.

2.2 Introduction

As mentioned in the Chapter I: Introduction to phosphirene chemistry the discovery of phosphirenes has been reported 1982 by Marinetti and Mathey.¹ The chemistry of phosphirenes has been actively developed since then. There are many more reports on this type of chemistry based on the characterization, synthesis, and chemical properties.² However, one problem has not been satisfactorily solved, the functionalization of phosphirenes at carbon. All of the described C-functional phosphirenes have been made by condensation of functional alkynes with phosphinidene units,^{1,3} and until now only one example has been published for the functionalization of phosphirene (Scheme 2.1).⁴ Deprotonation at carbon of phosphirene ring **60** using *n*BuLi, followed by trapping with acetone leads to new functionalized phosphirene **61**.

Scheme 2.1

In an attempt to solve this problem, we have decided to study the reactivity of 2-silyl- and 2-stannyl-substituted phosphirenes. To the best of our knowledge, there has been no report for the C-functionalization of these phosphirenes with other electrophiles. We describe our results in the following sections.

2.3 Results and Discussion

To probe the feasibility of the C-functional phosphirenes, we prepared the 2-silyl- and 2-stannyl-substituted phosphirenes in the coordination sphere of tungsten for convenience: the products are easier to synthesize and more stable. We first

synthesized the 7-phosphanorbornadiene complex **132** from phosphole **130** through a series of general transformation^{3ab} as shown in Scheme 2.2. Complexation of phosphole **130** with tungsten carbonyl, followed by [4+2] cycloaddition of the phosphole complex **131** thus obtained with dimethylacetylene dicarboxylate gives the 7-phosphanorbornadiene complex **132** in high yield.

Scheme 2.2

Upon heating, the generated $[PhP-W(CO)_5]$ **133** from 7-phosphanorbornadiene precursor **132** was treated with $PhCCSiMe_3$ to give the expected 2-silylphosphirene **134** in 87% yield (Scheme 2.3).

Scheme 2.3

Much attention has been paid to a structure of 2-silylphosphirene **134**. Surprisingly, the X-ray crystal structure (Figure 2.1) shows a lot of disorder, but the key parameters of the ring remain reliable as shown in Table 2.1.

Figure 2.1 Molecular structure of 2-silylphosphirene **134**.

Table 2.1 Selected bond lengths (Å) and angles (°) for 2-silylphosphirene **134**.

Bond lengths (Å)		Bond angles (°)	
Si(1)–C(6)	1.884(5)	C(7)–C(6)–P(1)	67.7
C(6)–C(7)	1.319(5)	C(7)–C(6)–Si(1)	148.7
C(6)–P(1)	1.812(4)	P(1)–C(6)–Si(1)	143.5
C(7)–C(8)	1.446(9)	C(6)–C(7)–C(8)	148.5
C(7)–P(1)	1.791(5)	C(6)–C(7)–P(1)	69.4
C(17)–P(1)	1.819(2)	C(8)–C(7)–P(1)	142.2

The most significant finding is that the P–C(Si) bond is elongated by comparison with the other P–C ring bond (1.812(4) and 1.843(1) vs 1.791(5) and

1.763(1) Å). This elongation could have a steric origin since both P and C are substituted by bulky groups (SiMe_3 , $\text{W}(\text{CO})_5$, Ph); we also considered the electronic effect of silyl substituent from DFT calculation, we observed that this elongation is reproduced by the computed structure of the 2-silyl-1,3-dimethylphosphirene $\text{W}(\text{CO})_5$ complex at the B3LYP/6-31 G(d)-Lanl2dz (W) level. In this case, the bulkiness of the substituents would hardly explain the lengthening of the P–C(Si) bond so we favor the electronic effect. The most interesting point of the computation concerns the shape of the LUMO as shown in Figure 2.2.

Figure 2.2 LUMO of 2-silyl-1,2-dimethylphosphirene pentacarbonyl tungsten complex as computed by DFT at the B3LYP/6-31G(d)-Lanl2dz (W) level.

From calculation result, it shows a significant presence of electron density at phosphorus but no presence at silicon. We are planning to activate the C–Si bond of 2-silylphosphirene by using fluoride ion, and thus, this finding casts some doubt on the feasibility of this approach. Our initial experiments were carried out using 2-silylphosphirene **134** with nonstoichiometric amounts of TBAF in the presence of water or benzaldehyde, and we were delighted to find that the expected protonation

and functionalization do take place to give products. Protonation product **135** was obtained in 57% yield when we used 0.5 equiv. of TBAF at $-78\text{ }^{\circ}\text{C}$ to rt for 15 h. In the presence of benzaldehyde, we used 0.2 equiv. of TBAF under the same condition, we got **136** in 51% yield, and also protonation product **135** in 34% yield (Scheme 2.4). Obviously, these reactions are not under the control of the LUMO. It depends on the high affinity of silicon for F^- as the leading role.

Scheme 2.4

Phosphirene **135** is characterized by the expected high-field shift of its ^{31}P resonance at $\delta -156.6$ ppm in CD_2Cl_2 and its highly deshielded vinylic proton at $+8.48$ ppm with a $^2J_{\text{HP}}$ coupling of 21.0 Hz. Phosphirene **136** exists as a 1:1 mixture of two nonseparable diastereomers with their phosphorus resonances at high fields ($\delta\ ^{31}\text{P}$ -149.5 and -149.3 ppm in CD_2Cl_2). The ^{13}C spectrum of **136** shows the two sp^3 C–O resonances at $+72.5$ and $+72.8$ ppm which confirm to be CH(OH)Ph units.

In the presence of a stoichiometric equivalent of TBAF, the result was entirely different when operating at room temperature. We also observed a desilylation product, but it was followed by an attack of the fluoride ion at phosphorus with formation of the ring-opened vinylic phosphinous fluoride **137a**.

The resulting phosphinous fluoride **137a** was characterized by its ^{31}P resonance at very low fields ($\delta\ ^{31}\text{P}$ $+197.2$ ppm in CDCl_3), its huge $^1J_{\text{FP}}$ coupling of 850.0 Hz,

and its ^{19}F resonance at -132.8 ppm (PhCF_3). It was accompanied by a minor isomer **137b** ($\delta^{31}\text{P}$ +201.8 ppm in CDCl_3) whose formula was established by methanolysis (see later). The major product **137a** results from the preferential cleavage of the P–C(Ph) ring bond of **135** favored by the stabilizing effect of the phenyl substituent on the resulting carbanion, whereas the minor product comes from the cleavage of the P–CH bond. The formula of **137a** and **137b** were further ascertained by hydrolysis and methanolysis (Scheme 2.5).

Scheme 2.5

The hydrolysis product **138** shows the two expected vinylic carbons at 142.9 ($=\text{CHPh}$, $^2J_{\text{CP}} = 9.6$ Hz) and 129.0 ppm ($=\text{CHP}$, $^1J_{\text{CP}} = 34.5$ Hz). The CHPh proton shows a $^3J_{\text{PH}}$ coupling of 18.0 Hz, in agreement with an *E* geometry.⁵ The structural assignment of **139** is straightforward. More interesting is the structure of the minor product **139b** that we were able to get in the pure state. The key finding is that it contains a vinylic CH_2 carbon at 129.5 ppm ($^2J_{\text{CP}} = 14.4$ Hz). The interpretation of these results is as follows. At low temperature, the fluoride ion induces the desilylation of phosphirene **134** to give phosphirene **135**. Then, at room temperature, F^- attacks the phosphorus of **135** with preferential cleavage of the P–C(Ph) ring bond. This means

that this technique can be used for the functionalization of phosphirenes only at low temperature and with highly reactive co-reagents such as water and aldehydes.

The plausible mechanism for the formation of **137ab** is shown in Scheme 2.6. However, all attempts to isolation and purification of **137ab** failed due to the low stability of **137ab**.

Scheme 2.6

Furthermore, by treatment of phosphirene **134** with several electrophiles for example Iodomethane, Benzyl bromide, Benzoyl chloride, and 2-Bromothiophene in hope to functionalization the phosphirenes. To our disappointment, all attempts led us only to protonation product **135**.

Looking for the potential methods of functionalization of phosphirenes, we decided to prepare the 2-stannyl-substituted phosphirene **140** as shown in Scheme 2.7. The reaction of $[PhP-W(CO)_5]$ **133** as generated from the 7-phosphanorbornadiene precursor **132** with $PhCCSnBu_3$ in boiling toluene gives 2-stannylphosphirene **140** in 51% yield.

Scheme 2.7

We expected to use the 2-stannylphosphirene **140** thus obtained as a partner in a Stille cross-coupling reaction to react with various alkyl halides to get a variety of coupling products. In fact, we observed that **140** readily rearranges and is protonated to give the secondary alkynylphosphine **141** in the presence of the $[\text{PdL}_2]$ catalyst (Scheme 2.8). Secondary phosphine **141** displays a ^{31}P resonance at -59.9 ppm (CDCl_3) with a $^1J_{\text{HP}}$ coupling at 372.5 Hz. Its ^{13}C spectrum shows the two sp carbons at 109.2 ($^2J_{\text{CP}} = 13.4$ Hz) and 78.5 ppm ($^1J_{\text{CP}} = 82.4$ Hz). It appears that $[\text{PdL}_2]$ readily catalyzes the [1,3] shift of tin from carbon to phosphorus. This is not a real surprise since it is known that $\text{Pd}(0)$ readily inserts into the P–C ring bonds of phosphirenes **87** (Scheme 2.9).⁶

Scheme 2.8

Scheme 2.9

We know that copper can catalyzed the cross-coupling reaction, so next idea came out by preparing PhCCCu to react with the [PhP–W(CO)₅] **133**, generated from the 7-phosphanorbornadiene precursor **132**. But no desired 2-cuprophosphirene **143** was obtained because the PhCCCu readily helps the decomposition of phosphanorbornadiene complex **132** to give phosphinidene complex **133** and as we use PhCCCu in situ which contains a small amount of water. We found only oxidation product⁷ **142** even with the reaction at room temperature for 1 h (Scheme 2.10).

Scheme 2.10

We described the synthesis of 2-silylphosphirene **134** from the reaction of [PhP–W(CO)₅] and PhCCSiMe₃. By continuing this research, we decided to perform the reaction of phosphanorbornadiene complex **132**, as a precursor of [PhP–W(CO)₅], with Me₃Si(CC)₃SiMe₃ in boiling toluene. Whatever ratios of phosphanorbornadiene complex **132** and Me₃Si(CC)₃SiMe₃, we always got only the monophosphirene **144** in moderate yield (Scheme 2.11). No bis- or tris- condensation products were obtained. Phosphirene **144** shows a characteristic peak at $\delta^{31}\text{P}$ –146.3 ppm in CDCl₃ with $^1J_{\text{PW}}$ = 280.5 Hz.

Scheme 2.11

The next attempted approach to functionalize the phosphirene ring was to use PhCCSO_2Ph as a trapping reagent (Scheme 2.12). Indeed, we know that the nucleophilic addition of Grignard reagent or alkyl lithium onto the sulfonyl group of $\text{PhCCS}(\text{O})_2\text{Tol}$ leads to the displacement products. So if we use this technique with phosphirene, we might be able to get functionalized products. The reaction of phosphinidene complex, generated from phosphanorbornadiene complex **132**, and PhCCSO_2Ph was carried out in toluene at 110 °C for 6 h. 2-Sulfonylphosphirene **145** was generated in 68% yield. The resulting phosphirene **145** was characterized by its ^{31}P resonance at high fields ($\delta^{31}\text{P} -108.8$ ppm in CDCl_3 with $^1J_{\text{PW}} = 280.5$ Hz).

Scheme 2.12

However, when we tried the reaction of 2-sulfonylphosphirene with various metallic reagents, for example vinyl magnesium bromide, isopropyl magnesium bromide, $n\text{-BuLi}$, or MeLi at -78 °C in THF, we were unable to detect the expected phosphirene products. We only observed complex mixtures on ^{31}P NMR because the metallic reagents not only attack at sulfonyl group but also at the phosphorus center, leading to the cleavage of the ring.

2.4 Conclusion

From this series of experiments, it clearly appears that the functionalization of performed phosphirenes is a very tricky problem. Even mild nucleophilic functionalization methodologies are limited by the competing nucleophilic ring opening promoted by the significant localization of LUMO at P. On the other hand, electrophilic methodologies have not produced any useful results until now, and catalytic methodologies are limited by the easy activation of the P–C ring bonds. More work is obviously needed to solve this problem.

2.5 Experimental

General Information:

NMR spectra were obtained on Bruker AV 500, BBFO1, BBFO2 or JEOL ECA400 and ECA 400SL spectrometer. All spectra were recorded at 298K. The chemical shift is given as dimensionless δ values and is frequency referenced relative to tetramethylsilane for ^1H and ^{13}C NMR spectroscopy. The ^{31}P NMR and ^{13}C NMR report as proton decoupled NMR spectra. In ^{13}C NMR spectra, the descriptors *cis* and *trans* (CO) refer to the position of carbonyl groups with respect to P. The Elemental Analysis Laboratory of the Division of Chemistry and Biological Chemistry at Nanyang Technological University of Singapore performed elemental analyses. HRMS spectra were obtained in ESI mode on a Finnigan MAT95XP HRMS system (Thermo Electron Corp.). X-ray crystallographic analyses were performed on a Bruker X8 APEX diffractometer. All reactions were performed using standard schlenk techniques under argon. Silica gel (230-400 mesh) was used for the chromatographic purifications. All the commercially available chemicals were used without prior drying or purification.

2.5.1 Preparation of 1-phenyl-3,4-dimethylphosphole (131)^{3a}

131

To a stirred suspension of tungsten carbonyl (10.55 g, 30.0 mmol) in 20 mL CH₃CN, was added Me₃NO.2H₂O (3.35 g, 30.0 mmol) in small portions during 30 min. The yellow solution was stirred for further 30 min and evaporated to dryness under vacuum. The crude W(CO)₅(CH₃CN) thus obtained was dissolved in dry THF 20 mL. Phosphole **130** (5.00 g, 26.6 mmol) was added to a solution at 0 °C and stirred for 15 h. After evaporation, the residue was chromatographed on silica gel with 100% hexane as eluent and later hexane/ethyl acetate (50:50) to give pale yellow product **131** (10.5 g, 77% yield). ³¹P NMR (162 MHz, CDCl₃): δ +10.6 (s, ¹J_{PW} = 214.7 Hz). ¹H NMR (400 MHz, CDCl₃): δ 7.49-7.36 (m, 5H, ArH), 6.47 (d, ²J_{PH} = 37.1 Hz, 2H, 2×CH), 2.18 (s, 6H, 2×CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 199.1 (d, *J* = 18.2 Hz, *trans* CO), 196.3 (dt, *J* = 63.0, 5.8 Hz, *cis* CO), 150.6 (2×C–P), 150.5 (2×C–CH₃), 131.3 (d, *J* = 11.5 Hz, 2×CH), 130.4 (d, *J* = 5.7 Hz, *ipso* C), 129.9 (CH), 128.9 (d, *J* = 10.5 Hz, 2×CH), 17.4 (CH₃), 17.3 (CH₃).

2.5.2 Preparation of 1-phenylphosphanorbornadiene complex (132)^{3a}

132

1-Phenyl-3,4-dimethylphosphole complex (**131**) (1.02 g, 2.00 mmol) was dissolved in 5 mL of toluene and dimethyl acetylenedicarboxylate (0.95 mL, 7.81 mmol) was added dropwise. The mixture was heated at 85 °C for overnight. After

evaporation, the residue was chromatographed on silica gel with 100% hexane and then hexane/ethyl acetate (80:20) to give a yellow solid **132** (0.975 g, 75% yield). ^{31}P NMR (162 MHz, CDCl_3): δ +208.8 (s, $^1J_{\text{PW}} = 236.6$ Hz). ^1H NMR (400 MHz, CDCl_3): δ 7.36-7.14 (m, 5H, ArH), 3.97 (s, 2H, $2\times\text{CH}$), 3.64 (s, 6H, $2\times\text{OCH}_3$), 2.03 (s, 6H, $2\times\text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3): δ 198.7 (d, $J = 25.8$ Hz, *trans* CO), 195.8 (d, $J = 6.7$ Hz, *cis* CO), 168.3 (COOCH_3), 164.8 (COOCH_3), 145.8 (d, $J = 5.7$ Hz, $=\text{C}(\text{CO}_2\text{Me})$), 141.2 ($=\text{C}(\text{CO}_2\text{Me})$), 141.1 ($=\text{C}(\text{CH}_3)$), 140.3 ($=\text{C}(\text{CH}_3)$), 138.0 (d, $J = 16.2$ Hz, *ipso* C), 130.1 (CH), 129.8 ($2\times\text{CH}$), 129.5 ($2\times\text{PCH}$), 128.3 (d, $J = 29.6$ Hz, $2\times\text{CH}$), 59.7 (d, $J = 20.0$ Hz, OCH_3), 52.4 (d, $J = 17.2$ Hz, OCH_3), 19.7 (CH_3), 16.1 (CH_3).

2.5.3 Preparation of 2-silylphosphirene **134**

134

The 7-phosphanorbornadiene complex **132** (0.30 g, 0.458 mmol) and trimethyl(phenylethynyl)silane (0.240 g, 1.37 mmol) in 5 mL of toluene was heated at 110 °C for 15 h. After evaporation, the residue was chromatographed on silica gel with 100% hexane as eluent to give crystals of **134** (0.242 g, 87% yield). ^{31}P NMR (162 MHz, CDCl_3): δ -177.5 (s, $^1J_{\text{PW}} = 273.6$ Hz). ^1H NMR (400 MHz, CDCl_3): δ 7.75 (d, $J = 6.9$ Hz, 2H, ArH), 7.55-7.48 (m, 3H, ArH), 7.40-7.32 (m, 5H, ArH), 0.38 (s, 9H, $3\times\text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3): δ 198.0 (d, $J = 31.6$ Hz, *trans* CO), 196.3 (d, $J = 8.6$ Hz, *cis* CO), 145.7 (d, $J = 16.3$ Hz, $=\text{C}(\text{Ph})$), 139.1 (d, $J = 11.5$ Hz, *ipso* C(PhP)), 131.7 (d, $J = 35.5$ Hz, $=\text{C}-\text{SiMe}_3$), 131.2 (CH(PhP)), 131.2 (CH(PhP)), 131.1 (CH(PhP)), 130.6 (CH(PhP)), 130.6 (CH), 130.1 (CH), 129.4 ($2\times\text{CH}(\text{PhP})$), 128.5 (CH), 128.4 (CH), 127.6 (d, $J = 7.7$ Hz, *ipso* C(PhC)), -0.70 ($3\times\text{CH}_3$). The ^{13}C

assignments were made by comparison with previous data.⁸ Ana. Calcd for $C_{22}H_{19}O_5PSiW$: C, 43.58; H, 3.16. Found: C, 43.69; H, 3.61.

2.5.4 General procedure for the preparation of compounds **135** and **136**

2.5.4.1 2-Phenylmethanol-1,3-diphenylphosphirene (**136**)

136

2-Trimethylsilyl-1,3-diphenylphosphirene tungsten complex (**134**) (0.235 g, 0.387 mmol) was dissolved in 5 mL of THF, and benzaldehyde (0.041 g, 0.387 mmol) was then added. 1M solution of tetra-*n*-butylammonium fluoride (TBAF) (0.08 mL, 0.08 mmol) was added dropwise to the mixture at -78°C and stirred at room temperature. After evaporation, the residue was chromatographed on silica gel with 100% hexane as eluent and later hexane/ethyl acetate (90:10) to give **136** as a pale yellow solid (0.126 g, 51% yield) and **135** as a brown solid (71.0 mg, 34% yield). **136**: ^{31}P NMR (162 MHz, CD_2Cl_2): δ -149.5 and -149.3 (d, $J_{\text{PW}} = 269.0, 282.0$ Hz). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.78-7.76 (m, 2H, ArH, minor isomer), 7.73-7.70 (m, 2H, ArH, major isomer), 7.52-7.47 (m, 12H, ArH, mixture of two isomers), 7.42-7.35 (m, 4H, ArH, mixture of two isomers), 7.33-7.23 (m, 10H, ArH), 6.25 (d, $J = 2.8$ Hz, 1H, CH-Ph), 6.18 (d, $J = 5.0$ Hz, 1H, CH-Ph), 2.68 (br s, 2H, $2\times\text{OH}$). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 198.6 and 198.5 (2d, $J = 29.6, 30.5$ Hz, *trans* CO), 196.7 and 196.6 (2d, $J = 18.1$ Hz, *cis* CO), 140.5 (d, $J = 8.6$ Hz, $=\text{C}(\text{Ph})$), 138.9 (2d, $J = 5.7, 8.6$ Hz, $=\text{C}(\text{CH})$), 133.9 (2d, $J = 13.4$ Hz, *ipso* C(PhP)), 131.8 (CH), 131.7 (CH), 131.5 (CH), 131.3 (CH), 131.1 (CH), 130.9 (CH), 129.7 (CH), 129.5 (CH), 129.4 (CH), 129.2 (CH), 129.1 (CH), 129.0 (CH), 128.9 (CH), 128.8 (CH), 127.1 (d, $J = 28.6$ Hz,

CH(Ph)), 126.3 (d, $J = 5.7$ Hz, *ipso* C(Ph–C=C)), 72.7 (br, CH–OH), 72.4 (br, CH–OH), Exact mass: calcd for C₂₆H₁₇O₆PW 640.0272, found: 640.0264.

2.5.4.2 1,3-Diphenylphosphirene (135)

135

2-Trimethylsilane-1,3-phenylphosphirene (**134**) (0.02 g, 0.033 mmol) was dissolved in 2 mL of THF and 1M TBAF (0.017 mL, 0.017 mmol) was added into the reaction flask. Three drops of water were added to the mixture at -78 °C and stirred for overnight to room temperature. After evaporation, the residue was chromatographed on silica gel with 100% hexane as eluent to give **135** as a brown solid (10.0 mg, 57% Yield). ³¹P NMR (162 MHz, CDCl₃): δ -156.6 (s, $^1J_{PW} = 273.6$ Hz). ¹H NMR (400 MHz, CDCl₃): δ 8.47 (d, $J = 21.0$ Hz, 1H, CH), 7.84-7.80 (m, 2H, ArH), 7.58-7.50 (m, 5H, ArH), 7.47-7.40 (m, 3H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 198.2 (d, $J = 31.5$ Hz, *trans* CO), 196.2 (td, $J = 62.0, 8.6$ Hz, *cis* CO), 138.29 and 138.27 (dd, $J = 9.6$ Hz, =CPh + *ipso* PhP), 131.6 (CH), 131.4 (CH), 130.8 (CH), 130.5 (d, $J = 3.8$ Hz, CH), 129.3 (CH), 129.0 (CH), 128.6 (d, $J = 10.5$ Hz, CH), 127.4 (CH), 126.0 (*ipso* C), 125.93 (d, $J = 6.7$ Hz, *ipso* C), 125.2 (CH), 117.6 (d, $J = 6.7$ Hz, CH). Anal. Calcd for C₁₉H₁₁O₅PW: C, 42.73; H, 2.08. Found: C, 43.11; H, 1.74.

2.5.5 General procedure for the preparation of compounds **137a,b** and **138**

2.5.5.1 Alkenylfluorophosphine (**137ab**)

137ab

2-Trimethylsilyl-1,3-diphenylphosphirene (**134**) (15.2 mg, 0.025 mmol) was dissolved in 2 mL of THF and 1M TBAF (0.025 mL, 0.025 mmol) was added dropwise at -78°C and stirred for 1 h at room temperature. After evaporation, the crude product **137ab** (ratio 54:46) were obtained as dark brown oil. All attempted to purify **137ab** failed due to the low stability of this complexes. ^{31}P NMR (162 MHz, CDCl_3): δ +197.2 (dd, $^1J_{\text{PF}} = 850.1$ Hz, $^1J_{\text{PW}} = 324.3$ Hz) and +201.8 (dd, $^1J_{\text{PF}} = 850.1$ Hz, $^1J_{\text{PW}} = 324.3$ Hz). ^{19}F NMR (376 MHz, CDCl_3 , PhCF_3): -132.8 (d, $^1J_{\text{PF}} = 839.7$ Hz).

2.5.5.2 Alkenylphosphinous acid (**138**)

138

2-Trimethylsilyl-1,3-diphenylphosphirene (**134**) (0.103 g, 0.17 mmol) was dissolved in 5 mL of THF and 1M TBAF (0.17 mL, 0.17 mmol) was added dropwise at -78°C and stirred for 1 h at room temperature. After evaporation, the residue was chromatographed on silica gel with hexane/ethyl acetate (90:10) to obtain **138** as a white solid (26.0 mg, 28% yield). ^{31}P NMR (162 MHz, CD_2Cl_2): δ +101.6 (s, $^1J_{\text{PW}} = 280.5$ Hz). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.67-7.62 (m, 2H, ArH), 7.52-7.45 (m, 5H, ArH), 7.38-7.34 (m, 3H, ArH), 7.14 (dd, $J = 18.8, 17.4$ Hz, 1H, $=\text{CHPh}$), 6.84 (dd, $J =$

22.9, 17.4 Hz, 1H, =CHP), 4.00 (br s, 1H, OH). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 199.7 (d, $J = 24.0$ Hz, *trans* CO), 196.5 (td, $J = 64.2, 8.62$ Hz, *cis* CO), 142.9 (d, $J = 9.6$ Hz, =CHPh), 140.5 (d, $J = 46.9$ Hz, *ipso* C(PhP)), 135.1 (d, $J = 15.3$ Hz, *ipso* C(Ph)), 130.7 (CH), 129.9 (CH), 129.1 (d, $J = 40.2$ Hz, =CHP), 128.9 (2 $\times$ CH), 128.9 (CH), 128.8 (CH), 128.7 (CH), 128.7 (CH), 127.6 (2 $\times$ CH). Anal. Calcd for $\text{C}_{19}\text{H}_{13}\text{O}_6\text{PW}$: C, 41.33; H, 2.37. Found: C, 40.91; H, 2.77.

2.5.6 General procedure for the preparation of compounds **139a** and **139b**

2-Trimethylsilyl-1,3-diphenylphosphirene (**134**) (0.121 g, 0.20 mmol) was dissolved in 5 mL of THF and 2 mL of MeOH was added to the reaction. 1M TBAF (0.20 mL, 0.20 mmol) was added dropwise at -78°C and stirred for 1 h at room temperature. After evaporation, the residue was chromatographed on silica gel with hexane/ethyl acetate (80:20) to give **139a** (37.0 mg, 33% yield) and **139b** (13.0 mg, 11% yield).

2.5.6.1 Alkenylphosphinite **139a**

139a

^{31}P NMR (162 MHz, CDCl_3): δ +117.6 (s, $^1J_{\text{PW}} = 284.8$ Hz). ^1H NMR (400 MHz, CDCl_3): δ 7.62-7.39 (m, 10H, ArH), 7.29 (t, $J = 17.5$ Hz, 1H, CHPh), 6.80 (t, $J = 17.5$ Hz, 1H, CHP), 3.55 (d, $J = 12.8$ Hz, 3H, OCH_3). ^{13}C NMR (100 MHz, CDCl_3): δ 199.9 (d, $J = 25.9$ Hz, *trans* CO), 196.6 (td, $J = 65.2, 8.6$ Hz, *cis* CO), 146.9 (d, $J = 13.4$ Hz, CH), 138.5 (d, $J = 46.0$ Hz, C), 135.2 (d, $J = 16.3$ Hz, C), 130.9 (CH), 130.3 (CH), 129.7 (CH), 129.6 (CH), 129.2 (2 $\times$ CH), 129.0 (CH), 128.9 (CH), 127.9 (2 $\times$ CH), 125.7 (d, $J = 38.3$ Hz, CH), 54.3 (d, $J = 6.7$ Hz, OCH_3). Exact mass: Calcd. For $\text{C}_{20}\text{H}_{15}\text{O}_6\text{PW}$: 566.0116. Found: 566.0106.

2.5.6.2 Alkenylphosphinite 139b

139b

^{31}P NMR (162 MHz, CDCl_3): δ +125.9 (s, $^1J_{\text{PW}} = 284.8$ Hz). ^1H NMR (400 MHz, CDCl_3): δ 7.66-7.61 (m, 2H, ArH), 7.50-7.44 (m, 3H, ArH), 7.24-7.17 (m, 3H, ArH), 7.08-7.06 (m, 2H, ArH), 6.18 (d, $J = 32.0$ Hz, 1H, =CH *trans* P), 6.14 (d, $J = 16.0$ Hz, 1H, =CH *cis* P), 3.50 (d, $J = 13.7$ Hz, 3H, OCH_3). ^{13}C NMR (100 MHz, CDCl_3): δ 198.8 (d, $J = 27.8$ Hz, *trans* CO), 196.9 (td, $J = 10.2, 7.7$ Hz, *cis* CO), 148.6 (d, $J = 32.6$ Hz, C), 137.9 (d, $J = 13.4$ Hz, C), 137.1 (d, $J = 42.2$ Hz, C), 131.1 (CH), 130.8 (CH), 130.7 (CH), 129.5 (d, $J = 14.4$ Hz, CH_2), 128.8 (CH), 128.6 (CH), 128.3 (2 $\times$ CH), 128.26 (CH), 128.15 (CH), 128.12 (CH), 53.9 (OCH_3). Exact mass: Calcd. For $\text{C}_{20}\text{H}_{15}\text{O}_6\text{PW}$: 566.0116, found 566.0109.

2.5.7 Preparation of 2-tributylstannyl-1,3-diphenylphosphirene (140)

140

The 7-phophanorbonadiene complex (**132**) (1.96 g, 3.00 mmol) and tributyl(phenylethynyl)stannane (2.35 g, 6.00 mmol) in 10 mL of toluene were heated at 110 °C for 15 h. After evaporation, the residue was chromatographed on silica gel with 100% hexane as eluent to give **140** as a brown solid (1.26 g, 51% yield). ^{31}P NMR (162 MHz, CDCl_3): δ -179.9 (s, $^1J_{\text{PW}} = 273.5$ Hz). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.93 (d, $J = 6.9$ Hz, 2H, ArH), 7.65-7.54 (m, 5H, ArH), 7.43 (br s, 3H, ArH), 1.76-1.70 (m, 6H, 3 $\times$ CH_2), 1.50-1.41 (m, 12H, 3 $\times$ CH_2CH_2), 0.98 (t, $J = 3.0$ Hz, 9H,

$3\times\text{CH}_3$). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 199.2 (d, $J = 30.6$ Hz, *trans* CO), 197.4 (d, $J = 8.6$ Hz, *cis* CO), 148.6 (d, $J = 14.4$ Hz, C), 141.0 (d, $J = 7.7$ Hz, C), 133.1 (C), 132.7 (C), 132.2 (CH), 132.1 (CH), 131.6 (CH), 130.7 (CH), 130.5 ($2\times\text{CH}$), 130.0 ($2\times\text{CH}$), 129.0 (CH), 128.9 (CH), 29.9 (t, $J = 22.0$ Hz, $3\times\text{CH}_2$), 28.1 (t, $J = 59.4$ Hz, $3\times\text{CH}_2$), 14.2 ($3\times\text{CH}_3$), 12.4 ($3\times\text{CH}_2$). Anal. Calcd for $\text{C}_{31}\text{H}_{37}\text{O}_5\text{PSnW}$: C, 45.23; H, 4.53. Found: C, 45.62; H, 4.02.

2.5.8 Preparation of Alkynylphosphine **141**

141

The catalyst was prepared from $\text{Pd}(\text{dba})_2$ (16.4 mg, 0.03 mmol) and PPh_3 (15.8 mg, 0.06 mmol) in toluene (10 mL). After 10 min of stirring at room temperature, phosphirene **140** (0.54 g, 0.66 mmol) was added. The mixture was then heated at 120 °C for 3 h. After evaporation of the solvent, purification on silica gel with hexane/ethyl acetate (80:20) gave **141** as a yellow solid (0.114 g, 32% yield). ^{31}P NMR (162 MHz, CDCl_3): δ -59.9 (dd, $^1J_{\text{PH}} = 372.5$ Hz, $^1J_{\text{PW}} = 236.7$ Hz). ^1H NMR (400 MHz, CDCl_3): δ 7.76-7.71 (m, 2H, *ArH*), 7.57-7.49 (m, 5H, *ArH*), 7.42-7.38 (m, 3H, *ArH*), 6.48 (d, $^1J_{\text{PH}} = 372.0$ Hz, 1H, *PH*). ^{13}C NMR (100 MHz, CDCl_3): δ 199.0 (d, $J = 23.0$ Hz, *trans* CO), 195.9 (d, $J = 6.7$ Hz, *cis* CO), 132.6 ($2\times\text{CH}$), 131.2 (CH), 131.1 (CH), 131.0 (CH), 130.9 (CH), 130.4 (CH), 129.7 (C), 129.3 (CH), 129.2 (CH), 128.7 ($2\times\text{CH}$), 128.0 (d, $J = 4.8$ Hz, C), 109.2 (d, $J = 13.4$ Hz, C), 78.5 (d, $J = 82.4$ Hz, C). Exact mass: Calcd. For $\text{C}_{19}\text{H}_{11}\text{O}_5\text{PW}$: 533.9853, found 533.9865.

2.5.9 Preparation of phenylphosphinous acid **142**

142

The 7-phosphanorbonadiene complex **132** (0.20 g, 0.306 mmol) and phenylethynyl cuprate (50.0 mg, 0.306 mmol) in 3 mL of toluene were stirred at room temperature for 1 h. After evaporation, the residue was chromatographed on silica gel with 100% hexane as eluent then with hexane/ethyl acetate (70:30) to give **142** as colorless oil (71.1 mg, 52 % yield). ^{31}P NMR (162 MHz, CDCl_3): δ +84.4 (s, $^1J_{\text{PW}} = 276.1$ Hz, $^1J_{\text{PH}} = 359.3$ Hz). ^1H NMR (400 MHz, CD_2Cl_2): δ 8.27 (d, $^1J_{\text{PH}} = 357.2$ Hz, 1H, *PH*), 7.66 (m, 2H, *ArH*), 7.53-7.49 (m, 3H, *ArH*), 1.58 (br s, 1H, *OH*).

2.5.10 Preparation of phosphirene **144**

144

The 7-phosphanorbornadiene complex **132** (0.600 g, 0.86 mmol) and $\text{Me}_3\text{Si}(\text{CC})_3\text{SiMe}_3$ (0.124 g, 0.57 mmol) in 5 mL of toluene was heated at 110 °C for 24 h. After evaporation of the solvent the residue was chromatographed on silica gel by using 100% hexane to give **144** (0.122 g, 33 % yield). ^{31}P NMR (202 MHz, CDCl_3): δ -146.9 (s, $^1J_{\text{PW}} = 280.5$ Hz). ^1H NMR (400 MHz, CDCl_3): δ 7.41-7.34 (m, 5H, *ArH*), 0.33 (s, 9H, SiMe_3), 0.25 (s, 9H, SiMe_3). ^{13}C NMR (100 MHz, CDCl_3): δ 197.5 (d, $J = 54.3$ Hz, *trans* CO), 195.7 (d, $J = 11.5$ Hz, *cis* CO), 148.7 (d, $J = 60.0$ Hz, C), 138.2 (d, $J = 9.3$ Hz, C), 134.4 (d, $J = 21.7$ Hz, C), 131.3 (CH), 131.1 (CH), 130.8 (CH), 128.7 (CH), 128.5 (CH), 101.9 (C), 97.03 (d, $J = 4.7$ Hz, C), 86.7 (C),

63.5 (d, $J = 12.4$ Hz, C), -0.54 (SiMe₃), -1.31 (SiMe₃). Exact mass: calcd for C₂₃H₂₃O₅PSi₂W 650.0331, found: 650.0337.

2.5.11 Synthesis of phosphirene **145**

145

The 7-phosphanorbornadiene complex **132** (0.131 g, 0.20 mmol) and PhCCSO₂Ph (48.5 mg, 0.20 mmol) in 5 mL of toluene was heated at 110 °C for 15 h. After evaporation of the solvent the residue was chromatographed on silica gel by using hexane/CH₂Cl₂ (50:50) to give phosphirene **145** (91.8 mg, 68% yield). ³¹P NMR (162 MHz, CDCl₃): δ -108.9 (s, $^1J_{\text{PW}} = 280.5$ Hz). ¹H NMR (400 MHz, CDCl₃): δ 8.04-7.97 (m, 4H, ArH), 7.71-7.67 (m, 1H, ArH), 7.65-7.61 (m, 1H, ArH), 7.59-7.54 (m, 4H, ArH), 7.48-7.42 (m, 3H, ArH), 7.38-7.34 (m, 2H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 196.7 (d, $J = 34.5$ Hz, *trans* CO), 194.8 (d, $J = 8.6$ Hz, *cis* CO), 143.5 (d, $J = 13.4$ Hz, C), 139.7 (d, $J = 4.8$ Hz, C), 135.9 (d, $J = 10.5$ Hz, C), 134.8 (CH), 133.5 (CH), 133.0 (2×CH), 131.6 (CH), 131.2 (CH), 131.1 (CH), 129.8 (2×CH), 129.6 (2×CH), 128.8 (CH), 128.7 (CH), 128.2 (d, $J = 16.3$ Hz, C), 128.1 (2×CH), 124.0 (C). Exact mass: calcd for C₂₅H₁₅O₇PSW 673.9785, found: 673.9790.

2.6 References

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CHAPTER 3

Synthesis, structure, and chemistry of 2-amino-substituted phosphirenes

3.1 Overview

The reaction of the bulky ynamine $\text{PhCCN}^i\text{Pr}_2$ with terminal phosphinidene complexes $[\text{R}-\text{PW}(\text{CO})_5]$, generated from phosphanorbornadiene complex, affords the corresponding phosphirenes for $\text{R} = \text{Ph}$ and OMe and the diphosphetene for $\text{R} = \text{Me}$. The structure of 1-phenylphosphirene shows elongated $\text{P}-\text{C}(\text{N})$ and $\text{C}=\text{C}$ ring bonds. The reaction of this phosphirene with dimethyl acetylenedicarboxylate gives the phosphole resulting from the insertion of the alkyne into the $\text{P}-\text{C}(\text{N})$ bond and the tetrafunctional arene resulting from $[2+2+2]$ cycloaddition of one alkyne with two phosphirene units.

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3.2 Introduction

Inspired by Marinetti and Mathey's report in 1984 on the reaction of terminal phosphinidene complexes with enamines. This reaction proceeds via the decomposition of phosphanorbornadiene complex **132** with 1-morpholinoisobutene at 110–120 °C to give the expected 2-aminophosphirane intermediate **146**, which can easily be hydrolyzed upon reaction with water, generating an open-chain structure **147** (Scheme 3.1).¹ From these results, we noticed that the chemistry of the three-membered cycle of 2-amino-substituted phosphirane **146** is highly perturbed by the amino substituents.

Scheme 3.1

Since the amino substituents present in phosphirane sharply destabilizes the P–C(N) ring bond and ring-opening takes place very easily upon treatment with water leading to a phosphine complex **147**, we decided to investigate the behavior of 2-aminophosphirenes. It would be quite interesting to determine whether the phosphirene ring would give a similar phenomenon. In fact, the delocalization of the nitrogen lone pair over the C=C double bond of phosphirene induces a completely

different type of chemistry. A related investigation of this chemistry has been performed by Averin et al. 2-Amino-substituted iminophosphirenes were prepared by condensation of iminophosphines with ynamines.² However, it is known that pentavalent phosphirenes show a high propensity to ring-opening³ and that their chemistry is quite different from that of trivalent phosphirenes. We investigated the possibility for the synthesis of 2-amino-substituted phosphirenes.

3.3 Results and Discussion

Once again, we explored the chemistry of these 2-aminophosphirenes in the coordination sphere of tungsten for convenience since the products are easier to synthesize and more stable. In a preceding work by Hoa and Mathey in 1990,⁴ based on the well-established generation of $[\text{PhP}-\text{W}(\text{CO})_5]$ from phosphanorbornadiene complex **132**, the reaction of $[\text{PhP}-\text{W}(\text{CO})_5]$ with MeCCNEt_2 afforded the phosphole complex **148**, most likely through a $[1+2+2]$ cycloaddition between the phosphinidene complex and the molecules of aminoalkynes. However, the authors observed an intermediate with a ^{31}P signal at $\delta -133.0$ ppm, corresponding to a phosphirene complex. Unfortunately, it proved impossible to isolate this complex as it readily inserts a second molecule of aminoalkyne to give phosphole **148** (Scheme 3.2).

Scheme 3.2

Since it was impossible to get the phosphirene complex with MeCCNEt_2 , we decided to investigate this reaction further using the more bulky isopropyl substituents and the slightly less electron-rich ynamine $\text{PhCCN}^i\text{Pr}_2$.⁶ A general procedure for the

synthesis of $\text{PhCCN}^i\text{Pr}_2$ is shown in Scheme 3.3.⁵⁻⁶ This reaction proceeds in two steps, first, the in situ formation of the 1,1-difluoro alkene **149** from benzaldehyde, triphenylphosphine, and sodium chlorodifluoroacetate. Then, by reacting the alkene thus obtained with 2 equiv. of lithium diisopropylamine the ynamine **150** ($\text{PhCCN}^i\text{Pr}_2$) is obtained in good yield.

Scheme 3.3

We started our investigation by the reaction of $[\text{RP}-\text{W}(\text{CO})_5]$ and $\text{PhCCN}^i\text{Pr}_2$ in boiling toluene. To our delight, the desired phosphirene complexes were obtained as shown in Scheme 3.4. When $\text{R} = \text{Ph}$ and $\text{R} = \text{OMe}$, the phosphirene products were produced in 54% and 68% yield, respectively.

Scheme 3.4

The presence of the three-membered ring phosphirenes in **151** and **152** is obvious from the ^{31}P chemical shifts at high fields: **151**, $\delta -141.0$ ($^1J_{\text{PW}} = 271.6$ Hz) and **152**, $\delta -56.1$ ($^1J_{\text{PW}} = 325.6$ Hz). Based on our previous results,⁷ the phosphirene complex generated from the methoxyphosphinidene unit and diphenylacetylene gives

^{31}P chemical shift at -61.4 ($^1J_{\text{PW}} = 266.0$ Hz). It should be noted that, there is a significant influence on the chemical shift, when replacing the phenyl by the N^iPr_2 substituent, but no marked difference in terms of the $^1J_{\text{PW}}$ coupling constants. We know that the magnitude of these couplings depends on the donor-acceptor properties of phosphorus.⁸ Thus the above observation suggests that there is only a limited electronic interaction between the amino substituent and phosphorus in these species. The ^{13}C NMR spectrum shows the huge polarization of the $\text{C}=\text{C}(\text{N})$ double bond, for example for **152**: δ C(Ph) 102.6 (s), C(N) 141.5 (d, $^1J_{\text{CP}} = 22.9$ Hz). Much attention has been paid to the structure of these amino-substituted phosphirenes, as determined by the X-ray analysis of phosphirene **151**. The molecular structure of **151** and the selected bond lengths ($\text{\AA}$) and angles ($^\circ$) are provided in Figure 3.1 and Table 3.1, respectively.

Figure 3.1 X-ray crystal structure analysis of phosphirene **151**.

Table 3.1 Selected bond lengths (Å) and angles (°) for 2-aminophosphirene **151**.

Bond lengths (Å)		Bond angles (°)	
C(7)–N(1)	1.332(4)	C(7)–C(8)–P(1)	69.42(2)
C(7)–C(8)	1.343(4)	C(8)–C(7)–P(1)	66.47(2)
C(7)–P(1)	1.806(3)	C(7)–P(1)–C(8)	44.12(1)
C(8)–P(1)	1.768(3)	C(7)–C(8)–C(9)	150.0(3)
C(8)–C(9)	1.457(4)	C(8)–C(7)–N(1)	146.7(3)
C(15)–P(1)	1.833(3)	P(1)–C(7)–N(1)	146.6(3)

The X-ray crystallography studies firstly revealed that the P–C(N) ring bond (1.806 Å) is significantly longer than the P–C(Ph) bond (1.768 Å), implying rather easy ring opening or insertions. Secondly, the nitrogen is planar ($\Sigma\text{C}–\text{N}–\text{C}$ angles 358.5°), suggesting a strong delocalization of the lone pair over the ring. Thirdly, the short N–C connecting bond (1.332 Å) confirms this delocalization. Lastly, the C=C double bond of this phosphirene ring (1.343 Å) is sizably elongated when compared to that of the triphenylphosphirene pentacarbonyltungsten complex⁹ (1.307 Å), implying the possibility of enamine reactivity. We shall report hereafter on this dual reactivity, by using DFT at the B3LYP/6-31G(d)-Lanl2dz(W) level to calculate the structure of [1-methyl-2-dimethylaminophosphirene]pentacarbonyl tungsten. We found that the computed structure is close to the X-ray structure of **151**. The two highest occupied orbitals are shown in Figure 3.2. The highest corresponds to the antisymmetric combination of the two P–C ring bonds, while the next one depicts the conjugation between the p lone pair at nitrogen with the C=C π bond.

Figure 3.2 Higher occupied Kohn-Sham orbitals of 1-methyl-2-dimethylamino phosphirene pentacarbonyltungsten complex as computed by DFT.

In the late 20th century, Averin et al.² have described that, in some cases, the reaction of iminophosphines with ynamines yields a 1,2-diphosphetene. Another observation that is of great interest is the reaction of $[\text{MeP}-\text{W}(\text{CO})_5]$ with $\text{PhCCN}^i\text{Pr}_2$. Whatever ratios of phosphinidene units and ynamine, we always obtained the diphosphetene (**155**) as the sole important product in up to 57% yield (Scheme 3.5).

Scheme 3.5

As expected, this product shows two nonequivalent phosphorus nuclei at δ -0.8 and $+28.0$ ppm with a very small P–P coupling of 8.7 Hz, which is characteristic for this type of ring.¹⁰ Thus confirming our initial establishment for the diphosphetene structure, we hereby performed the X-ray diffraction study of **155**. The molecular

structure of **155** is displayed in Figure 3.3. The selected bond lengths (Å) and angles (°) are provided in Table 3.2.

Figure 3.3 X-ray crystal structure analysis of the diphosphetene **155**.

Table 3.2 Selected bond lengths (Å) and angles (°) for the diphosphetene **155**.

Bond lengths (Å)		Angles (°)	
P(1)–P(2)	2.2185(9)	P(1)–P(2)–C(1)	77.35(9)
P(1)–C(8)	1.872(3)	P(2)–P(1)–C(8)	76.00(9)
P(2)–C(1)	1.809(3)	P(1)–C(8)–C(1)	101.5(2)
C(1)–C(8)	1.381(4)	P(2)–C(1)–C(8)	104.3(2)
C(8)–N(1)	1.353(4)	C(15)–P(1)–P(2)–C(21)	164.26
P(1)–C(15)	1.835(3)	C(1)–C(8)–P(1)–P(2)	7.37

The nitrogen lone pair and the C=C double bond of the ring show a significant conjugation with planar nitrogen, short N–C connecting bond with the ring, elongated

C=C double bond. The ring is slightly non planar with $C1-C8-P1-P2 = 7.37^\circ$. Moreover, the two Me-P substituents are in a *trans* disposition. Based on the previous literature as shown in Scheme 3.6^{11,12}

Scheme 3.6

When an alkynyl substituent is grafted on one carbon of the cycle, a similar insertion of a phosphinidene unit into the phosphirene ring was observed. However, we have to demonstrate why this insertion exclusively takes place with the methylphosphinidene complex and why, in this case, we get the *trans* R-P-P-R product whereas, in the previous cases described in the literature, only or mainly the *cis* product was obtained. In order to know on what side of phosphirene (P-C(Ph) or P-C(N)) the insertion takes place, we decided to investigate the reaction of **155** with **151**, but we could not obtain the expected insertion product. In the alkynyl case, the insertion takes place on the side of the elongated bond substituted by the sterically small triple bond. If we admit the same regiochemistry, the presence, in our case, of the very bulky diisopropylamino group might explain the change of stereochemistry. If we use the level of the LUMO of phosphinidenes as a probe for their electrophilicity,

then DFT computations at the B3LYP/6-31G(d)-Lanl2dz level indicate that the electrophilicity decreases in the order $[\text{MeP-Cr(CO)}_5] > [\text{PhP-Cr(CO)}_5] > [\text{MeOP-Cr(CO)}_5]$. The ring expansion would take place only with the most electrophilic species in the tungsten case.

Having in hand a 2-aminophosphirene **151**, this encouraging finding prompted us to check whether it was possible to insert an external alkyne unit into the phosphirene ring to get a series of amino-substituted phospholes. As far as we know, the chemistry of this type of phosphole has not been described in the literature.¹³ Unfortunately, in our attempt, we were unable to detect the expected product when diphenylacetylene in boiling toluene for 15 h was used. It means that the stability of **151** is very high in contrast with the very high reactivity of 2-aminophosphiranes.¹ Much attention has been devoted to this 2-aminophosphirene **151**; we got unexpected results with the electrophilic dimethyl acetylenedicarboxylate (Scheme 3.7). The reaction of 2-aminophosphirene **151** with 2 equiv. of dimethyl acetylenedicarboxylate was carried out in boiling toluene for 15 h. Unexpected arene **158** and phosphole **159** were obtained in 24% and 50% yield, respectively.

Scheme 3.7

Figure 3.4 X-ray crystal structure analysis of arene **158**.

Table 3.3 Selected bond lengths (Å) and angles (°) for arene **158**.

Bond lengths (Å)		Dihedral angles (°)	
C(1)–C(2)	1.393(4)	C(1)–C(2)–C(9)–O(3)	60.70
C(2)–C(3)	1.389(4)	C(2)–C(1)–C(7)–O(1)	114.07
C(3)–C(4)	1.402(4)	C(1)–C(6)–N(2)–C(32)	91.05
C(4)–C(5)	1.423(4)	C(6)–C(5)–C(23)–C(24)	169.52
C(5)–C(6)	1.415(4)	C(5)–C(4)–N(1)–C(20)	87.78
C(6)–C(1)	1.395(4)	C(4)–C(3)–C(11)–C(12)	108.10
C(4)–N(1)	1.432(4)		
C(6)–N(2)	1.421(4)		

The X-ray crystal structure analysis, the selected bond lengths (Å), and angles (°) of arene **158** are presented in Figure 3.4 and Table 3.3. The C–C bonds of the arene ring are significantly nonequivalent between 1.389(4) and 1.423(4) Å. The ring is

slightly distorted with $C1-C6-C4-C3 = 3.24^\circ$. All of the substituents are tilted out of the ring plane to reduce steric congestion. According to the ^{13}C NMR spectrum, the rotation of the phenyl substituents is blocked. To the best of our knowledge, there have been no reports on this type of hexasubstituted arene.

The mechanism for the formation of arene **158** is depicted in Scheme 3.8. It starts from the amino-induced nucleophilic addition reaction of phosphirene **151** with dimethyl acetylenedicarboxylate to give intermediate **160**. Then, addition of the intermediate thus generated to a second molecule of **151**, followed by cyclization and elimination of two phosphinidene units affords arene **158**. The driving force for this reaction is the aromaticity of the arene **158**.

The loss of phosphinidene complexes from phosphirane complexes has some precedents.¹⁴ We have here an example of reaction induced by the enamine subunit. The formation of the phosphole **159** is easier to explain: It involves the insertion of dimethyl acetylenedicarboxylate into the P–C(N) ring bond of phosphirene ring. Its formula is proposed on the basis of its ^{13}C NMR spectrum. The three carbons connected to phosphorus give resonance at 145.9 ($J = 37.2$ Hz, C–CO₂Me), 134.6 ($J = 35.3$ Hz, *C ipso*-PhP), and 127.4 ($J = 39.1$ Hz, P–C-Ph). The high shielding and coupling of the ring carbon substituted by the phenyl group implies that the amino group occupies the β position on the ring. The carbon bearing the amino group appears at 157.5 with a coupling of 9.5 Hz. In addition, both the *ipso* and the *ortho* carbons of the α -phenyl substituent are sizably coupled to phosphorus, by 14.3 and 10.5 Hz, respectively. Here, we have a clear example of insertion into the weak P–C(N) ring bond.

Scheme 3.8

3.4 Conclusion

This study clearly demonstrates that 2-aminophosphirenes have very different properties from 2-aminophosphiranes. The conjugation of the nitrogen lone pair with the double bond of the ring partly switch off the interaction between nitrogen and phosphorus through the P-C(N) ring bond, which governs the chemistry of 2-aminophosphiranes and induces a high propensity to ring-opening. This tendency does not exist to the same extent in the 2-aminophosphirenes, which are much more stable and react through both their enamine functionality and their P-C(N) ring bond.

3.5 Experimental

NMR spectra were obtained on Bruker AV 300, AV 400, AV 500, BBFO1, BBFO2 or JEOL ECA400 and ECA 400SL spectrometer. All spectra were recorded at 298K unless otherwise specified. The temperatures of samples in VT NMR experiments were calibrated by 4% methanol in methanol-*d*4. The chemical shift is given as dimensionless δ values and is frequency referenced relative to tetramethylsilane for ^1H and ^{13}C NMR spectroscopy. The ^{31}P NMR and ^{13}C NMR report as proton decoupled NMR spectra. In ^{13}C NMR spectra, the descriptors *cis* and *trans* (CO) refer to the position of carbonyl groups with respect to P. Elemental analyses were performed in the Division of Chemistry and Biological Chemistry, Nanyang Technological University, Singapore. HRMS spectra were obtained in ESI mode on a Finnigan MAT95XP HRMS system (Thermo Electron Corp.). X-ray crystallographic analyses were performed on a Bruker X8 APEX diffractometer. All reactions were performed under argon. Silica gel (230-400 mesh) was used for the chromatographic separations. All commercially available reagents were used as received from the suppliers.

3.5.1 General procedure for the preparation of compounds 151, 152 and 155

The 7-phosphanorbornadiene complex (0.084 mmol) and *N*-isopropyl-*N*-(phenylethynyl)propan-2-amine (34.0 mg, 0.168 mmol) were heated at 110 °C for 15 h in 1 mL of toluene. After evaporation of the solvent, the residue was chromatographed with hexane/ethyl acetate (90:10) to give the products.

3.5.1.1 Phosphirene 151

151

Yield: 35.0 mg, 54%. ^{31}P NMR (162 MHz, CDCl_3): δ -140.9 (s, $^1J_{\text{PW}} = 271.6$ Hz). ^1H NMR (400 MHz, CDCl_3): δ 7.55-7.48 (m, 4H, ArH), 7.40-7.35 (m, 5H, ArH), 7.25-7.21 (m, 1H, ArH), 3.89 (sep, 2H, $2\times\text{CH}$), 1.32 (d, $J = 6.8$ Hz, 6H, $2\times\text{CH}_3$), 1.19 (d, $J = 6.8$ Hz, 6H, $2\times\text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3): δ 200.4 (d, $J = 29.7$ Hz, *trans* CO), 198.6 (d, $J = 8.6$ Hz, *cis* CO), 141.3 (d, $J = 13.4$ Hz =C(N)), 133.8 (d, $J = 8.6$ Hz, *ipso* C(PhP)), 133.1 (d, $J = 15.3$ Hz, *ortho* CH(PhP)), 132.3 (s, *para* CH(PhP)), 132.0 (d, $J = 5.0$ Hz, *ipso* C(PhC)), 130.8 (s, *meta* CH(PhC)), 130.4 (d, $J = 10.6$ Hz, *meta* CH(PhP)), 130.0 (d, $J = 6.7$ Hz, *ortho* CH(PhC)), 128.2 (s, *para* CH(PhC)), 115.8 (s, =C(Ph)P), 53.9 ($2\times\text{CH}$), 24.5 ($2\times\text{CH}_3$), 24.0 ($2\times\text{CH}_3$). Anal. Calcd. for $\text{C}_{25}\text{H}_{24}\text{NO}_5\text{PW}$: C, 47.41; H, 3.82. Found: C, 47.62; H, 4.02.

3.5.1.2 Phosphirene 152

152

Yield: 40.0 mg, 68%. ^{31}P NMR (162 MHz, CD_2Cl_2): δ -56.1 (s, $^1J_{\text{PW}} = 325.6$ Hz). ^1H NMR (400 MHz, CD_2Cl_2 , -40 °C): δ 7.44-7.37 (m, 4H, ArH), 7.27-7.23 (t, $J = 7.1$ Hz, 1H, ArH), 4.19 (sep, 1H, CH), 3.77 (sep, 1H, CH), 3.12 (d, $J = 13.7$ Hz, 3H, OCH_3), 1.44 (d, $J = 6.4$ Hz, 3H, CH_3), 1.35 (dd, $J = 11.9, 6.6$ Hz, 6H, $2\times\text{CH}_3$), 1.26 (d, $J = 6.9$ Hz, 3H, CH_3). ^{13}C NMR (100 MHz, CD_2Cl_2 , -60 °C): δ 199.9 (d, $J = 37.2$ Hz, *trans* CO), 196.3 (d, $J = 9.5$ Hz, *cis* CO), 141.5 (d, $J = 22.9$ Hz, =C(N)), 131.3 (s, *ipso* C(Ph)), 128.9 (s, *meta* CH(Ph)), 127.8 (d, $J = 6.7$ Hz, *ortho* CH(Ph)), 126.8 (s, *para* CH(Ph)), 102.6 (s, =C(Ph)), 55.6 (CH), 52.1 (d, $J = 11.5$ Hz, OCH_3), 47.2 (CH), 25.7 (CH_3), 21.6 (CH_3), 21.4 (CH_3), 21.0 (CH_3). Anal. Calcd. for $\text{C}_{20}\text{H}_{22}\text{NO}_6\text{PW}$: C, 40.91; H, 3.78. Found: C, 40.25; H, 3.50.

3.5.1.3 Diphosphetene 155

155

Yield: 27.0 mg, 57%. ^{31}P NMR (162 Hz, CDCl_3): δ +28.0 (d, $^1J_{\text{PW}} = 230.0$ Hz, $^1J_{\text{PP}} = 8.7$ Hz), -0.83 (d, $^1J_{\text{PW}} = 230.0$ Hz, $^1J_{\text{PP}} = 8.7$ Hz). ^1H NMR (400 MHz, CDCl_3): δ 7.36-7.30 (m, 3H, ArH), 7.9 (d, $J = 7.3$ Hz, 2H, ArH), 3.90-3.83 (sep, 2H, $2\times\text{CH}$), 2.38 (dd, $J = 17.8, 5.5$ Hz, 3H, P- CH_3), 2.24 (dd, $J = 17.8, 5.5$ Hz, 3H, P- CH_3), 1.24 (d, $J = 6.8$ Hz, 6H, $2\times\text{CH}_3$), 1.19 (d, $J = 6.8$ Hz, 6H, $2\times\text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3): δ 198.2 (d, $J = 23.9$ Hz, *trans* CO), 197.6 (d, $J = 23.9$ Hz, *trans* CO), 196.1 (d, $J = 5.7$ Hz, *cis* CO), 195.9 (d, $J = 6.7$ Hz, *cis* CO), 150.1 (dd, $J = 38.1, 22.9$ Hz, $=\text{C}-\text{N}$), 137.8 (dd, $J = 15.3, 8.6$ Hz, *ipso* C(Ph)), 129.0 ($2\times\text{CH}$), 128.9 (m, *ortho* and *meta* CH(Ph)), 128.3 (*para* CHPh), 116.1 (dd, $J = 42.0, 20.4$ Hz, $=\text{C}(\text{Ph})$), 52.2 (d, $J = 4.8$ Hz, $2\times\text{CH}$), 26.8 (dd, $J = 10.5, 8.6$ Hz, P- CH_3), 24.0-23.7 (m, P- CH_3 , $2\times\text{CH}_3$), 21.7 ($2\times\text{CH}_3$). Anal. Calcd. for $\text{C}_{26}\text{H}_{25}\text{NO}_{10}\text{P}_2\text{W}_2$: C, 33.18; H, 2.68; N, 1.49. Found: C, 33.10; H, 1.94; N, 1.27.

3.5.2 Reaction of 2-aminophosphirene 151 with dimethyl acetylenedicarboxylate

Complex **151** (60.0 mg, 0.094 mmol) and dimethyl acetylenedicarboxylate (27.0 mg, 0.188 mmol) were heated at 110 °C in 1 mL of toluene for 15 h. After evaporation of the solvent, the residue was chromatographed with hexane/ethyl acetate (90:10) to give **158** as a colorless crystal and **159** as an orange solid.

3.5.2.1 Arene 158

158

Yield: 6.2 mg, 24%. ^1H NMR (400 MHz, CDCl_3): δ 7.32-7.27 (m, 10H, ArH), 3.75 (s, 3H, CO_2CH_3), 3.35 (s, 3H, CO_2CH_3), 3.16 (sep, 2H, $2\times\text{CH}$), 3.00 (sep, 2H, $2\times\text{CH}$), 0.79 (d, $J = 6.5$ Hz, 6H, $2\times\text{CH}_3$), 0.73 (d, $J = 6.5$ Hz, 6H, $2\times\text{CH}_3$), 0.56 (d, $J = 6.5$ Hz, 6H, $2\times\text{CH}_3$), 0.51 (d, $J = 6.5$ Hz, 6H, $2\times\text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3): δ 169.0 (CO), 168.5 (CO), 150.7 (C), 149.2 (C), 146.3 (C), 141.1 (C), 140.0 (C), 135.9 (C), 135.7 (C), 133.7 (C), 131.3 ($2\times\text{CH}$), 130.2 (CH), 129.3 (CH), 128.2 (CH), 127.5 (CH), 127.4 (CH), 127.1 (CH), 127.0 (CH), 126.7 (CH), 52.0 (OCH_3), 51.9 (OCH_3), 50.9 ($2\times\text{CH}$), 50.3 ($2\times\text{CH}$), 22.6 ($2\times\text{CH}_3$), 22.3 ($2\times\text{CH}_3$), 21.9 ($2\times\text{CH}_3$), 21.8 ($2\times\text{CH}_3$). Anal. Calcd. for $\text{C}_{34}\text{H}_{44}\text{N}_2\text{O}_4$: C, 74.97; H, 8.14. Found: C, 75.08; H, 7.75.

3.5.2.2 Phosphole 159

159

Yield: 37.0 mg, 50%. ^{31}P NMR (162 MHz, CD_2Cl_2): δ +24.5 (s, $^1J_{\text{PW}} = 245.4$ Hz). ^1H NMR (400 MHz, CDCl_3): δ 7.62-7.57 (m, 3H, ArH), 7.50-7.46 (m, 3H, ArH), 7.24-7.13 (m, 4H, ArH), 3.96 (s, 3H, CO_2CH_3), 3.63 (s, 3H, CO_2CH_3), 3.49-3.42 (sep, 2H, $2\times\text{CH}$), 1.16 (d, $J = 6.6$ Hz, 6H, $2\times\text{CH}_3$), 1.00 (d, $J = 6.6$ Hz, 6H, $2\times\text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3): δ 197.8 (d, $J = 23.9$ Hz, *trans* CO), 195.8 (d, $J = 6.7$ Hz, *cis*

CO), 166.1 (d, $J = 16.2$ Hz, α -COO), 161.8 (d, $J = 11.5$ Hz, β -COO), 157.5 (d, $J = 9.5$ Hz, $=C(N)$), 148.0 (d, $J = 16.2$ Hz, β -C(COOMe)), 145.9 (d, $J = 37.2$ Hz, α -C(COOMe)), 134.5 (d, $J = 35.5$ Hz, *ipso* C(PhP)), 133.8 (d, $J = 14.3$ Hz, *ipso* C(PhC)), 132.7 (d, $J = 13.4$ Hz, *ortho* CH(PhP)), 131.7 (d, $J = 1.9$ Hz, *para* CH(PhP)), 129.5 (d, $J = 10.5$ Hz, *ortho* CH(PhC)), 129.3 (d, $J = 5.7$ Hz, *meta* CH(PhC)), 128.9 (*para* CH(PhC)), 128.4 (*meta* CH(PhP)), 126.3 (d, $J = 39.1$ Hz, P-C(Ph)), 53.0 (OCH₃), 52.3 (OCH₃), 51.2 (2 $\times$ CH-N), 23.6 (2 $\times$ CH₃), 22.2 (2 $\times$ CH₃). Exact mass: calcd for C₃₁H₃₀NO₉PW, 774.1161; found, 774.1141. Anal. Calcd. for C₃₁H₃₀NO₉PW: C, 48.02; H, 3.90; N, 1.81. Found: C, 47.62; H, 3.78; N, 1.89.

3.6 References

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CHAPTER 4

Serendipitous discovery of a phosphirene-phosphindole rearrangement

4.1 Overview

The reaction of strong Lewis acids with 2-amino-3-phenylphosphirene pentacarbonyltungsten complexes leads to the corresponding 2-amino phosphindoles through the unexpected formation of a bond between phosphorus and one of the *ortho* carbons of the phenyl ring.

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4.2 Introduction

We have come across the 2-aminophosphirenes in Chapter 3 of this thesis. According to the Hückel rule $[(4n+2)\pi]$, the smallest possible P-aromatic structure is a three-membered ring, occupied by 2π electrons and a vacancy. However, there are only very few distinct examples of this electronic configuration. The first reported example is the discovery of phosphirenylium cation, by Regitz in 1994 (Scheme 4.1). They explored the phosphirenylium cation **19** as a free species obtained by reaction of phosphirene **34** with a strong Lewis acid. Later on in 1999, the same authors demonstrated that not only free phosphirene species but also P-W(CO)₅ complex of phosphirenes are to the phosphirenylium cation (Scheme 4.2).² In spite of its 2π aromaticity,³ this cation appears to be quite difficult to make and must be kept in liquid SO₂ at low temperature. Since then, there has been no report on this type of chemistry.

Scheme 4.1

Scheme 4.2

The reasons for our renewed intent in these species lied in the puzzling instability of this 2π -aromatic system. We wanted to increase the stabilizing the system following the same approach as Bertrand did for the stabilization of cyclopropylidene, an isoelectronic structure of phosphirenylium cation, which was stabilized using amino substituents. Following our work on 2-aminophosphirenes as

described in Chapter 3,⁵ we decided to investigate the reaction further by the potential conversion of 1,2-diaminophosphirenes into 2-aminophosphirenylium cations. This research led us to the discovery of a completely unexpected rearrangement of 2-amino-3-phenylphosphirenes into 2-aminophosphindoles through the formation of a bond between phosphorus and one of the *ortho* carbons of the phenyl ring. We shall discuss this point more thoroughly later in this account.

4.3 Results and discussion

Throughout this work, our starting product was 1-aminophosphirene tungsten complex **166**⁶ that can be readily prepared from phosphanorbornadiene complex **163** (Scheme 4.3). As usual for this kind of strained phosphorus-carbon heterocycles, we decided to work in the coordination sphere of tungsten for convenience. The products are easier to synthesize and more stable. The reaction of β -chloroethynylphosphinidene complex, generated from the phosphanorbornadiene complex precursor **163**, with aniline was carried out in the presence of CuCl as a catalyst to give the β -chloroethyl(phenylamino)phosphane **164** in high yield. The resulting phosphane thus obtained was cyclized by using *n*-BuLi, affording 1-phenyl aminophosphirane **166**.

Scheme 4.3

The reaction of $[\text{PhNHP-W(CO)}_5]$ as generated from **166** as mentioned above with $\text{PhCCN}^i\text{Pr}_2$ was performed in boiling toluene. It led us to the expected 1,2-diaminophosphirene (**168**) in good yield (Scheme 4.4).

Scheme 4.4

As expected, phosphirene **168** shows high-field shift of the ^{31}P resonance at -97.8 ppm ($^1J_{\text{PW}} = 306.8$ Hz, $^2J_{\text{PNH}} = 26.3$ Hz). Our initial attempt to convert 1,2-diaminophosphirene **168** into the corresponding phosphirenylium cation **169** (Figure 4.1) was performed using a strong Lewis acid such as the commercially available tris(pentafluorophenyl)borane to abstract the amino substituent attach to phosphorus. Surprisingly, we found a completely unexpected ring expansion compound **170** (Scheme 4.5) because of water containing tris(pentafluorophenyl)borane. So if we can use water-free tris(pentafluorophenyl)borane, we could get the expected phosphirenylium cation **170**. The plausible mechanism for the formation of **170** is shown in Scheme 4.6.

Figure 4.1

Scheme 4.5

Scheme 4.6

The structure of the 2-aminophosphindole (**170**) was established by X-ray crystal structure analysis (Figure 4.2). The selected bond lengths ($\text{\AA}$) and angles ($^\circ$) are provided in Table 4.1. In fact, it is known that commercial tris(pentafluorophenyl)borane contains water and behaves as a strong protic acid.⁸ It is clear that the first step of the reaction is a protonation of the nitrogen substituent at phosphorus, leading to a replacement of the P–N by the P–O bond. But the unexpected and puzzling finding is that another reaction takes place converting the phosphirene into the phosphindole ring.

Figure 4.2 X-ray crystal structure analysis of phosphindole **170**.

Table 4.1 Selected bond lengths (Å) and angles (°) for phosphindole **170**.

Bond lengths (Å)		Bond angles (°)	
P(1)–O(6)	1.559(9)	C(6)–P(1)–C(13)	89.53(9)
P(1)–C(6)	1.815(2)	C(6)–P(1)–O(6)	113.19(9)
P(1)–C(13)	1.895(2)	C(13)–P(1)–O(6)	108.26(9)
C(13)–N(1)	1.292(3)	P(1)–C(13)–N(1)	127.68(2)
C(13)–C(12)	1.502(3)	C(12)–C(13)–N(1)	122.82(2)
C(12)–C(11)	1.507(3)		
C(6)–C(11)	1.398(3)		

In order to avoid the perturbing effect of water, we decided to use another approach to the synthesis of phosphirenylium ion relying on the AlCl_3 -induced dealkylation of 1- β -chloroethylphosphirenes.^{2,9} Preliminary experiments were carried out with the phosphanorbornadiene complex **163** and $\text{PhCCN}^i\text{Pr}_2$ in boiling toluene. They generated not only 1- β -chloroethylphosphirene **171** but also 1,2-diphosphetene **172** in moderate yields.

Scheme 4.6

The resulting phosphirene **171** was then treated with AlCl_3 at room temperature and led to the immediate formation of the corresponding phosphindole **173**. No phosphirenylium cation was observed, and the β -chloroethyl substituent at phosphorus remained intact. The identification of **173** was essentially carried out by NMR spectroscopy. Particularly significant are the single ethylenic proton at 5.86 ppm ($J_{\text{PH}} = 22.5$ Hz) and the CH_2Cl carbon at 39.0 ppm ($J_{\text{CP}} = 6.6$ Hz) in CDCl_3 . We also used the already described (in chapter 3), 2-aminophosphirenes ($\text{R} = \text{Ph}, \text{Me}$)⁵ to demonstrate the generality of this ring expansion. Phosphindoles **173-175** were obtained in moderated yields (Scheme 4.7).

Scheme 4.7

The molecular structure of phosphindole **174** was characterized by X-ray crystal structure analysis (Figure 4.3). The selected bond lengths (Å) and angles (°) are revealed in Table 4.2. To the best of our knowledge, 2-aminophosphindoles were unknown until now, and thus, this easy transformation already has a synthetic interest. However, we were also puzzled by the fact that the *ortho* carbon of the phenyl substituent at C6 that becomes bonded to phosphorus is geometrically far away from this heteroatom in the starting phosphirene. A drastic distortion of the molecule is thus needed to create this bond.

In order to shed some light on this unprecedented rearrangement, we decided to study by DFT calculations the interaction between the aminophosphirene complex **176** and BH₃ (Figure 4.4), chosen as the simplest representative Lewis acid. We suspected that BH₃ might coordinate to the carbon bearing the phenyl substituent. The calculations were carried out at the B3LYP/6-31G(d)-lanl2dz (W) level. They indeed confirmed that a well defined adduct (**176**) is formed (no negative frequency). Its structure is shown in Figure 4. 5.

Figure 4.3 X-ray crystal structure analysis of phosphindole **174**.

Table 4.2 Selected bond lengths (Å) and angles (°) for phosphindole **174**.

Bond lengths (Å)		Bond angles (°)	
P(1)–C(6)	1.8032(1)	C(6)–P(1)–C(13)	91.34(6)
P(1)–C(13)	1.8503(1)	C(13)–N(1)–C(14)	120.36(1)
C(12)–C(13)	1.3672(2)	C(13)–N(1)–C(17)	121.90(1)
C(11)–C(12)	1.4459(2)	C(14)–N(1)–C(17)	116.35(1)
C(6)–C(11)	1.4019(2)		
C(13)–N(1)	1.3640(2)		

176**Figure 4.4** A structure between the aminophosphirene complex **176** and BH_3 . **Figure 4.5** Computed structure of **176** at the B3LYP/6-31+G(d)-lanl2dz(W) level.**Table 4.3** Significant distances (Å) and angles (°) for **176**.

Bond lengths (Å)		Bond angles (°)	
P(16)–C(1)	1.911	C(1)–P(16)–C(2)	44.48
P(16)–C(2)	1.804	P(16)–C(1)–C(28)	123.61
C(1)–C(2)	1.410	P(16)–C(1)–B(41)	111.77
C(1)–B(41)	1.755		
C(2)–N(7)	1.306		

The calculation results show that the B–C interaction is weak (1.76 vs 1.59 Å for the sum of the covalent radii) but sufficient to induce a sizable weakening of the corresponding P–C phosphirene bond, which is elongated from ca. 1.768 in the free species (X-ray)⁵ to 1.911 Å in **176**, and the development of a strong positive charge at phosphorus (Mulliken charge +0.63). On this basis, we suggest that the mechanism of the ring expansion involves the breaking of the P–C(Ph) phosphirene bond induced by the Lewis acid, followed by the electrophilic attack of P onto the *ortho* carbon of the phenyl ring (Scheme 4.8).

Scheme 4.8

We have one question to answer, what happens when no phenyl substituent is present on the phosphirene ring? To answer this question, we performed the reaction of phosphirane **166** with $^i\text{HexCCN}^i\text{Pr}_2$ in boiling toluene. 1,2-Diaminophosphirene **177** was obtained in 61% yield (Scheme 4.8). Under strictly identical conditions as for **174**, the 1,2-diaminophosphirene **177** reacts with tris(pentafluorophenyl)borane to give the borane-aniline adduct **178** in 61% yield and a mixture of two isomeric open-chain secondary phosphines (**179ab**) in 25% yield (Scheme 4.9).

Scheme 4.8

Scheme 4.9

The formula of **179** was established by X-ray crystal structure analysis. The two isomers of **179** (δ ^{31}P (**179a**) +68.8, $^1J_{\text{HP}}$ = 346.0 Hz, $^1J_{\text{PW}}$ = 298.1 Hz, major; δ ^{31}P (**179b**) +59.9, $^1J_{\text{HP}}$ = 337.0 Hz, $^1J_{\text{PW}}$ = 302.0 Hz, minor) *syn*-crystallize, but it is possible to extract from the X-ray data the structural parameters of **179a** that are presented in Figure 4.6. The formation of **179** can be explained as follows: after complexation by the Lewis acid and cleavage of the P–C(Hex) ring bond, the strongly positive phosphorus abstracts a hydride from the amino group. This observation confirms the results of the computation and establishes that the first step of the mechanism of the ring expansion of phosphirenes to phosphindoles is the cleavage of the P–C(Ph) ring bond. Besides, it cast a serious doubt on the possibility to use such a route to prepare amino-stabilized phosphirenylium ions.

Figure 4.6 X-ray crystal structure analysis of secondary phosphine complex **179a**.

Table 4.4 Selected bond lengths (Å) and angles (°) for phosphine complex **179a**.

Bond lengths (Å)		Bond angles (°)	
P(1)–C(13)	1.867(1)	O(1)–P(1)–C(13)	107.6(8)
P(1)–O(1)	1.63(2)	W(1)–P(1)–C(13)	109.1(4)
O(1)–B(1)	1.520(1)	W(1)–P(1)–O(1)	125.9(9)
C(13)–N(1)	1.471(1)	P(1)–C(13)–C(14)	127.5(9)
N(1)–C(25)	1.327(1)	P(1)–C(13)–N(1)	116.5(8)
N(1)–C(22)	1.520(1)	C(14)–C(13)–N(1)	116.0(9)
C(13)–C(14)	1.322(1)	C(13)–N(1)–C(22)	121.4(9)
		C(13)–N(1)–C(25)	118.4(1)
		C(22)–N(1)–C(25)	120.2(8)

4.4 Conclusion

At the moment, the synthesis of a stable phosphirenylium cation is far from being solved. Without amino substituents, it is unstable and must be kept in liq. SO₂. In our attempts to solve this problem, we used amino substituents to stabilize the ring. However, we found unexpected 2-aminophosphindoles upon treatment of 2-aminophosphirenes with strong Lewis acid. The reaction proceeds via the breaking of the P–C(Ph) bond induced by the Lewis acid, followed by the electrophilic attack of P

4.5 Experimental

NMR spectra were obtained on Bruker AV 300, AV 400, AV 500, BBFO1, BBFO2 or JEOL ECA400 and ECA 400SL spectrometer. All spectra were recorded at 298K unless otherwise specified. The temperatures of samples in VT NMR experiments were calibrated by 4% methanol in methanol-*d*₄. The chemical shift is given as dimensionless δ values and is frequency referenced relative to tetramethylsilane for ¹H and ¹³C NMR spectroscopy. The ³¹P NMR and ¹³C NMR report as proton decoupled NMR spectra. In ¹³C NMR spectra, the descriptors *cis* and *trans* (CO) refer to the position of carbonyl groups with respect to P. Elemental analyses were performed in the Division of Chemistry and Biological Chemistry, Nanyang Technological University, Singapore. HRMS spectra were obtained in ESI mode on a Finnigan MAT95XP HRMS system (Thermo Electron Corp.). X-ray crystallographic analyses were performed on a Bruker X8 APEX diffractometer. All reactions were performed under argon. Silica gel (230-400 mesh) was used for the chromatographic separations. All commercially available reagents were used as received from the suppliers.

4.5.1 Synthesis of β -chloroethynyl(phenylamino)phosphane **164**¹⁰

164

7- β -Chloroethynyl 7-phosphanorbornadiene complex (**163**) (1.11 g, 1.74 mmol) and aniline (0.16 mL, 1.74 mmol) in 15 mL of toluene were heated at 60 °C for 30 min in the presence of CuCl as a catalyst. After cooling and evaporation of toluene, the crude reaction mixture was chromatographed with hexane/ethyl acetate (90:10) to give product **164** (0.57 g, 64% yield). ³¹P NMR (162 MHz, CDCl₃): δ +1.5 (s, ¹J_{PW} = 254.0 Hz, ¹J_{PH} = 366.0 Hz). ¹H NMR (400 MHz, CDCl₃): δ 7.40-6.80 (m, 5H, ArH), 7.30-7.15 (m, ¹J_{PH} = 366.0 Hz, 1H, P-H), 4.02 (dd, ³J_{HH} = 7.3 Hz, 1H, N-H), 3.67 (m, 2H, CH₂P), 2.63 (m, 2H, CH₂Cl). ¹³C NMR (100 MHz, CDCl₃): δ 197.5 (d, *J* = 23.8 Hz, *trans* CO), 195.4 (d, *J* = 23.8 Hz, *cis* CO), 39.5 (s, CH₂Cl), 32.9 (d, *J* = 25.3 Hz, PCH₂).

4.5.2 Synthesis of 1-phenylaminophosphirane **166**¹⁰

166

Phosphane complex **164** (0.614 g, 1.20 mmol), in 15 mL of THF was cooled to -40 °C. 1.6 M *n*-BuLi (0.75 mL, 1.20 mmol) was added dropwise. The crude mixture was allowed to warm up to room temperature. After evaporation of THF, the residue was chromatographed with hexane/ethyl acetate (80:20) to afford phosphirane **166** (0.458 g, 80% yield). ³¹P NMR (162 MHz, CDCl₃): δ -132.0 (s, ¹J_{PW} = 288 Hz). ¹H NMR (400 MHz, CDCl₃): δ 7.24-6.88 (m, 5H, ArH), 3.97 (br s, 1H, NH), 1.63-1.17 (m, 4H, 2×CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 198.0 (d, *J* = 34.6 Hz, *trans* CO), 195.3 (d, *J* = 8.5 Hz, *cis* CO), 14.0 (d, *J* = 13.1 Hz, CH₂CH₂).

4.5.3 Preparation of phosphirene 168

168

The 1-aminophosphirane complex **166** (0.286 g, 0.60 mmol) and *N*-isopropyl-*N*-(phenylethynyl)propan-2-amine (0.242 g, 1.20 mmol) were heated in 5 mL of toluene at 100 °C for 2 h. After evaporation of the solvent, the residue was chromatographed with 100% hexane to give phosphirene **168** as colorless oil (0.238 g, 61%). ^{31}P NMR (162 MHz, CDCl_3): δ -97.8 (s, $^1J_{\text{PW}} = 306.8$ Hz, $^2J_{\text{PNH}} = 26.3$ Hz). ^1H NMR (400 MHz, CDCl_3 , -50 °C): δ 7.54-7.38 (m, 4H, *ArH*), 7.34-7.26 (m, 1H, *ArH*), 7.11 (d, $J = 7.4$ Hz, 2H, *ArH*), 6.90 (t, $J = 7.4$ Hz, 1H, *ArH*), 6.75 (d, $J = 7.8$ Hz, 2H, *ArH*), 4.23 (d, $J = 22.9$ Hz, 1H, *NH*), 4.04 (br sep, 1H, *CH*), 3.60 (br sep, 1H, *CH*), 1.35 (d, $J = 6.4$ Hz, 3H, CH_3), 1.32 (d, $J = 6.9$ Hz, 3H, CH_3), 1.11 (d, $J = 6.4$ Hz, 3H, CH_3), 1.04 (d, $J = 6.4$ Hz, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3 , -50 °C): δ 199.0 (d, $J = 33.5$ Hz, *trans* CO), 196.3 (d, $J = 8.6$ Hz, *cis* CO), 141.9 (d, $J = 11.5$ Hz, =C(N)), 136.2 (d, $J = 22.4$ Hz, *ipso* PhN) 130.9 (s, *ipso* ArC), 130.0 (4×ArCH), 127.9 (s, ArCH), 127.8 (s, ArCH), 126.4 (s, ArCH), 122.1 (s, ArCH), 120.0 (2× ArCH), 96.8 (d, $J = 9.6$ Hz, =C (ArC-P)), 54.3 (CH), 47.7 (CH), 25.5 (CH_3), 22.0 (CH_3), 21.5 (CH_3), 21.2 (CH_3). Exact mass: calcd. for $\text{C}_{25}\text{H}_{25}\text{N}_2\text{O}_5\text{PW}$: 648.1010; Found: 648.1016.

4.5.4 Preparation of phosphirene 177

177

The 1-aminophosphirane complex **166** (0.237 g, 0.50 mmol) and *N,N*-diisopropyloct-1-yn-1-amine (0.222 g, 1.00 mmol) were heated in 5 mL of toluene at 110 °C for 4 h. After evaporation of the solvent, the residue was chromatographed at – 5 °C with 100% hexane to give phosphirene **177** as colorless oil (0.204 g, 62%). ³¹P NMR (162 MHz, CDCl₃): δ –101.0 (s, ¹J_{PW} = 308.3 Hz). ¹H NMR (400 MHz, CDCl₃): δ 7.17 (t, *J* = 8.2 Hz, 2H, Ar*H*), 6.94 (t, *J* = 7.4 Hz, 1H, Ar*H*), 6.74 (d, *J* = 7.7 Hz, 2H, Ar*H*), 4.00 (d, ²J_{PH} = 22.7 Hz, 1H, NH), 3.74 (br s, 2H, 2×CH), 2.49-2.42 (m, 2H, CH₂), 1.67-1.59 (m, 2H, CH₂), 1.42-1.30 (m, 6H, 3×CH₂), 1.29-1.19 (m, 12H, 4×CH₃), 0.90 (t, *J* = 6.8 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 199.0 (d, *J* = 32.0 Hz, *trans* CO), 196.5 (d, *J* = 9.6 Hz, *cis* CO), 142.1 (d, *J* = 11.3 Hz, =C(N)), 137.7 (d, *J* = 12.1 Hz, *ipso* C(PhNH)), 128.7 (s, *meta* CH(Ph)), 121.9 (s, *ortho* CH(Ph)), 120.5 (s, *para* CH(Ph)), 98.4 (d, *J* = 2.5 Hz, =C), 31.4 (CH₂), 29.2 (CH₂), 28.3 (d, *J* = 3.6 Hz, CH₂), 26.8 (d, *J* = 3.1 Hz, CH₂), 22.5 (CH₂), 21.8 (4×CH₃), 14.0 (CH₃). Exact mass: calcd. for C₂₅H₃₃N₂O₅PW: 656.1636; Found: 656.1658.

4.5.5 General procedure for the preparation of complexes **171** and **172**

The 7-β-chloroethyl-7-phosphanorbornadiene complex **163** (0.320 g, 0.50 mmol) and *N*-isopropyl-*N*-(phenylethynyl)propan-2-amine (0.201 g, 1.00 mmol) were heated in 5 mL of toluene with a small amount of CuCl at 60 °C for 1 h. After evaporation of the solvent, the residue was chromatographed with hexane/ethyl acetate (90:10) to give phosphirene **171** (0.064 g, 21%) and diphosphetene **172** (0.054 g, 21%).

4.5.5.1 Phosphirene **171**

171

^{31}P NMR (122 MHz, CD_2Cl_2): δ -143.6 (s, $^1J_{\text{PW}} = 266.0$ Hz). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.54 (d, $J = 7.9$ Hz, 2H, *ortho* ArH), 7.43 (t, $J = 7.5$ Hz, 2H, *meta* ArH), 7.28 (t, $J = 6.7$ Hz, 1H, *para* ArH), 4.03 (sep, 2H, $2\times\text{CH}$), 3.45-3.36 (m, 2H, CH_2Cl), 2.42-2.34 (m, 2H, CH_2), 1.44 (d, $J = 6.8$ Hz, 6H, $2\times\text{CH}_3$), 1.39 (d, $J = 7.1$ Hz, 6H, $2\times\text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3): δ 193.8 (d, $J = 29.5$ Hz, *trans* CO), 196.4 (d, $J = 8.4$ Hz, *cis* CO), 141.3 (d, $J = 17.0$ Hz, $=\text{C}(\text{N})$), 130.6 (s, *ipso* ArC), 128.8 (s, *meta* ArCH), 127.9 (d, $J = 6.4$ Hz, *ortho* ArCH), 126.4 (s, *para* ArCH), 114.1 (s, $=\text{CP}$), 52.1 (CH), 52.0 (CH), 42.5 (d, $J = 13.2$ Hz, CH_2), 40.3 (CH_2), 22.5 ($2\times\text{CH}_3$), 22.0 ($2\times\text{CH}_3$). Exact mass: calcd for $\text{C}_{21}\text{H}_{23}\text{ClNO}_5\text{PW}$ 619.0512, found: 619.0523.

4.5.5.2 Diphosphetene 172

172

^{31}P NMR (162 MHz, CD_2Cl_2): δ +39.1 (d, $^1J_{\text{PW}} = 229.4$ Hz, $^1J_{\text{PP}} = 24.3$ Hz), 2.90 (d, $^1J_{\text{PW}} = 243.6$ Hz, $^1J_{\text{PP}} = 23.7$ Hz). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.43 (t, $J = 7.5$ Hz, 2H, ArH), 7.39-7.35 (m, 1H, ArH), 7.23 (t, $J = 8.2$ Hz, 2H, ArH), 3.91-3.87 (m, 4H, $2\times\text{CH}$, CH_2Cl), 3.86-3.82 (m, 2H, CH_2Cl), 3.26-3.10 (m, 2H, CH_2), 3.09-2.98 (m, 2H, CH_2), 1.37 (d, $J = 7.1$ Hz, 6H, $2\times\text{CH}_3$), 1.32 (d, $J = 6.7$ Hz, 6H, $2\times\text{CH}_3$). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 196.9 (d, $J = 26.1$ Hz, *trans* CO), 196.3 (d, $J = 26.8$ Hz, *trans* CO), 195.7 (d, $J = 5.8$ Hz, *cis* CO), 195.5 (d, $J = 6.7$ Hz, *cis* CO), 150.6 (dd, $J = 20.8$ and 33.0 Hz, P-C-N), 137.2 (d, $J = 9.5$ Hz, *ipso* ArC), 137.0 (d, $J = 10.2$ Hz, *ipso* ArC), 129.0 ($2\times\text{ArCH}$), 128.5 (ArCH), 128.4 (ArCH), 128.3 (ArCH), 114.8 (dd, $J = 20.0$ and 39.0 Hz, $=\text{CP}$), 53.7 (CH), 53.6 (CH), 43.8 ($2\times\text{CH}_2$), 41.0 ($2\times\text{CH}_2$), 23.6

(2×CH₃), 22.0 (2×CH₃). Exact mass: calcd for C₂₈H₂₇Cl₂NO₁₀P₂W₂ 1036.9506, found: 1036.9491.

4.5.6 Preparation of phosphindole complex **170**

170

Phosphirene **168** (9.0 mg, 0.014 mmol) was dissolved in 2 mL of CH₂Cl₂, and B(C₆F₅)₃ (11.0 mg, 0.021 mmol) was added into the reaction flask at 0 °C and the mixture was stirred for 30 min. After evaporation of the solvent, the residue was purified by flash column chromatography on silica gel with hexane/ethyl acetate (80:20) then CH₂Cl₂ to give **170** (7.0 mg, 46%) as white crystals. ³¹P NMR (162 MHz, CDCl₃): δ +98.9 (s, ¹J_{PW} = 311.1 Hz). ¹H NMR (400 MHz, CO(CD₃)₂): δ 7.61-7.58 (t, *J* = 7.6 Hz, 1H, ArCH), 7.46-7.39 (m, 3H, ArCH), 5.46 (m, 1H, CH(CH₃)₂), 4.95 (m, 1H, CH(CH₃)₂), 4.90-4.73 (m, 2H, CH₂), 1.84 (m, 9H, 3×CH₃), 1.14 (d, *J* = 6.4 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CO(CD₃)₂): δ 198.6 (d, *J* = 26.8 Hz, *trans* CO), 198.0 (br s, C=N+), 196.0 (d, *J* = 7.9 Hz, *cis* CO), 147.7 (br d, *J*_{CF} = 235.8 Hz, *ortho* ArCF), 139.1 (d, *J*_{CF} = 246.9 Hz, *para* ArCF), 139.3 (d, *J* = 45.9 Hz, benzo-CP), 136.6 (br d, *J* = 247.3 Hz, *meta* ArCF), 132.0 (br s, *ipso* CArB), 131.5 (s, ArCH), 128.0 (d, *J* = 10.0 Hz, ArCH), 127.8 (d, *J* = 17.6 Hz, ArCH), 125.6 (d, *J* = 4.0 Hz, ArCH), 64.6 (d, *J* = 6.9 Hz, NCH), 57.8 (s, NCH), 36.8 (d, *J* = 11.5 Hz, CH₂), 20.5, 18.8, 18.7, 18.2 (4×CH₃).

4.5.7 Model procedure for the preparation of phosphindoles **173**, **174**, and **175**

Phosphirene (0.10 mmol) was dissolved in 5 mL of CH₂Cl₂, and AlCl₃ (14.7 mg, 0.11 mmol) was then added and stirred at room temperature for 30 min. After evaporation of the solvent, CH₂Cl₂ was added and the solid was removed by filtration.

The residue was chromatographed on silica gel with hexane/ethyl acetate (80:20) to give phosphindole as white crystals.

4.5.7.1 Phosphindole 173

173

Yield: 25.0 mg (40%). ^{31}P NMR (162 MHz, CDCl_3): δ +5.2 (s, $^1J_{\text{PW}} = 228.2$ Hz, $^2J_{\text{PH}} = 22.5$ Hz). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.38 (t, $J = 7.6$ Hz, 1H, ArH), 7.27 (tt, $J = 7.6, 1.2$ Hz, 1H, ArH), 7.09 (d, $J = 7.6$ Hz, 1H, ArH), 7.08-7.05 (m, $J = 7.4, 3.5, 1.0$ Hz, 1H, ArH), 5.86 (d, $J = 22.5$ Hz, 1H, CH), 3.94 (sep, 2H, $2\times\text{CH}$), 3.40-3.32 (m, 1H, CHHCl), 3.09-3.01 (m, 1H, CHH), 2.73-2.70 (m, 2H, CH_2), 1.40 (d, $J = 6.7$ Hz, 6H, $2\times\text{CH}_3$), 1.38 (d, $J = 6.8$ Hz, 6H, $2\times\text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3): δ 198.2 (d, $J = 20.8$ Hz, *trans* CO), 196.1 (d, $J = 6.8$ Hz, *cis* CO), 153.7 (d, $J = 49.7$ Hz, P–C–N), 146.4 (d, $J = 9.6$ Hz, C–CP), 135.0 (d, $J = 50.6$ Hz, C–P), 131.0 (ArCH), 127.4 (d, $J = 15.2$ Hz, ArCH), 122.1 (d, $J = 10.2$ Hz, ArCH), 120.0 (d, $J = 5.1$ Hz, ArCH), 104.8 (d, $J = 14.2$ Hz, CH–CP), 52.6 (CH), 52.5 (CH), 39.0 (d, $J = 6.6$ Hz, CH_2), 35.6 (d, $J = 14.7$ Hz, CH_2), 20.6 ($2\times\text{CH}_3$), 20.0 ($2\times\text{CH}_3$). Exact mass: calcd for $\text{C}_{21}\text{H}_{23}\text{ClNO}_5\text{PW}$ 619.0512, found: 619.0518.

4.5.7.2 Phosphindole 174

174

Yield: 39.0 mg (62%). ^{31}P NMR (162 MHz, CDCl_3): δ +14.7 (s, $^1J_{\text{PW}} = 229.3$ Hz). ^1H NMR (400 MHz, CDCl_3): δ 7.62-7.57 (m, 2H, ArH), 7.45-7.37 (m, 3H, ArH),

7.22 (t, $J = 7.5$ Hz, 1H, ArH), 7.16-7.10 (m, 2H, ArH), 6.90 (td, $J = 8.0, 3.9$ Hz, 1H, ArH), 5.78 (d, $J = 22.4$ Hz, 1H, CH), 3.73 (sep, 2H, $2\times\text{CH}$), 1.33 (d, $J = 6.7$ Hz, 12H, $4\times\text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3): δ 198.2 (d, $J = 23.2$ Hz, *trans* CO), 196.4 (d, $J = 6.9$ Hz, *cis* CO), 155.9 (d, $J = 50.0$ Hz, P–C–N), 146.2 (d, $J = 13.6$ Hz, C–CP), 136.8 (d, $J = 52.3$ Hz, C–P), 133.2 (ArCH), 133.0 (ArCH), 131.3 (d, $J = 2.6$ Hz, ArCH), 130.6 (ArCH), 130.5 (d, $J = 36.4$ Hz, *ipso* ArC), 129.1 (ArCH), 129.0 (ArCH), 127.9 (d, $J = 14.5$ Hz, ArCH), 122.1 (d, $J = 10.9$ Hz, ArCH), 119.8 (d, $J = 3.8$ Hz, ArCH), 102.3 (d, $J = 11.1$ Hz, CH–CP), 50.4 (CH), 46.4 (CH), 20.3 ($2\times\text{CH}_3$), 19.8 ($2\times\text{CH}_3$). Exact mass: calcd for $\text{C}_{25}\text{H}_{24}\text{NO}_5\text{PW}$ 633.0901, found: 633.0904.

4.5.7.3 Phosphindole 175

175

Yield: 33 mg (56%). ^{31}P NMR (162 MHz, CDCl_3): δ +118.9 (s, $^1J_{\text{PW}} = 280.3$ Hz). ^1H NMR (400 MHz, CDCl_3): δ 7.38 (t, $J = 7.5$ Hz, 1H, ArH), 7.22 (t, $J = 7.6$ Hz, 1H, ArH), 6.99 (td, $J = 7.4, 4.0$ Hz, 1H, ArH), 6.93 (dd, $J = 7.6, 2.2$ Hz, 1H, ArH), 5.69 (d, $J = 22.9$ Hz, 1H, CH), 4.11 (br s, 2H, $2\times\text{CH}$), 3.37 (d, $J = 12.1$ Hz, 3H, OCH_3), 1.39 (d, $J = 6.8$ Hz, 6H, $2\times\text{CH}_3$), 1.35 (d, $J = 6.8$ Hz, 6H, $2\times\text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3): δ 198.7 (d, $J = 27.0$ Hz, *trans* CO), 196.1 (d, $J = 7.6$ Hz, *cis* CO), 155.4 (d, $J = 53.4$ Hz, P–C–N), 144.8 (d, $J = 14.3$ Hz, C–CP), 137.5 (d, $J = 48.7$ Hz, C–P), 132.5 (ArCH), 128.4 (d, $J = 17.6$ Hz, ArCH), 122.7 (d, $J = 7.6$ Hz, ArCH), 119.8 (d, $J = 2.9$ Hz, ArCH), 103.3 (d, $J = 18.1$ Hz, CH–CP), 55.3 (d, $J = 13.4$ Hz, OCH_3), 39.0 (CH), 29.8 (CH_3), 21.2 (CH_3). Exact mass: calcd for $\text{C}_{20}\text{H}_{22}\text{NO}_6\text{PW}$ 587.0694, found: C, 587.0696.

4.5.8 Aniline-borane adduct **178** and secondary phosphine complexes **179ab**.

Phosphirene **177** (0.145 g, 0.22mmol) was dissolved in 8 mL of CH₂Cl₂, B(C₆F₅)₃ (0.169 g, 0.33 mmol) was added into the reaction flask at 0 °C and the mixture was stirred for 30 min. After evaporation of the solvent, the residue was chromatographed on silica gel with hexane/ethyl acetate (80:20) to give the B–N adduct **178** then with CH₂Cl₂ to give **179ab**, both as white crystals.

4.5.8.1 Aniline-borane adduct **178**

178

Yield: 81.5 mg (61%). ¹H NMR (400 MHz, CDCl₃): δ 7.30-7.22 (m, 3H, overlapping *meta* and *para* ArCH), 7.20 (br s, 2H, NH₂), 7.08-7.02 (m, 2H, *ortho* ArCH). ¹³C NMR (100 MHz, CDCl₃): δ 147.7 (d, *J* = 238.0 Hz, *ortho* ArCF), 140.3 (d, *J* = 250.0 Hz, *para* ArCF), 137.2 (d, *J* = 247.0 Hz, *meta* ArCF), 134.3 (s, *ipso* ArC), 129.8 (s, 2×ArCH), 129.0 (s, ArCH), 122.4 (s, 2×ArCH), 116.1 (br s, BArC). ¹⁹F NMR (376 MHz, CDCl₃): δ −133.0 (d, ³*J*_{FF} = 20.0 Hz, 6F, *ortho* ArCF), −155.6 (t, ³*J*_{FF} = 21.4 Hz, 3F, *para* ArCF), −162.4 (td, ³*J*_{FF} = 24.4, 7.6 Hz, 6F, *meta* ArCF). Anal. Calcd for C₂₄H₇BF₁₅N: C, 47.64; H, 1.17; N, 2.31. Found: C, 47.65; H, 1.06; N, 2.31.

4.5.8.2 Phosphine complexes **179ab**

179ab

Yield: 60.2 mg (25%). ³¹P NMR (162 MHz, CDCl₃): δ +68.8 (s, ¹*J*_{PW} = 298.0 Hz, ¹*J*_{PH} = 346.2 Hz, major isomer), +59.9 (s, ¹*J*_{PW} = 302.4 Hz, ¹*J*_{PH} = 337.4 Hz, minor isomer). Selected ¹³C NMR data (400 MHz, CDCl₃, major isomer): δ 195.8 (d, *J* = 8.0

Hz, *cis* CO), 192.0 (s, C=N+), 147.8 (d, $J = 28.0$ Hz, =CH); ^{19}F NMR (376 MHz, CDCl_3): δ -132.3 (d, $^3J_{\text{FF}} = 23.1$ Hz, 6F, minor isomer of *ortho* ArCF), -132.6 (d, $^3J_{\text{FF}} = 24.7$ Hz, 6F, major isomer of *ortho* ArCF), -158.6 (t, $^3J_{\text{FF}} = 22.3$ Hz, 3F, minor isomer of *para* ArCF), -158.9 (t, $^3J_{\text{FF}} = 21.6$ Hz, 3F, major isomer of *para* ArCF), -164.4 (m, 6F, *meta* ArCF).

4.6 References

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CHAPTER 5

Miscellaneous research

5.1 Overview

Among all the phosphirene chemistry reported to date, considerable attention has been directed towards not only the development of new synthetic methods but also of new chemistry. In this chapter we report on the work that we have done on this phosphirene chemistry including the synthesis of 1-vinylphosphirenes, the functionalization of phosphirenes, and the chemistry of phosphirene sulfides.

5.2 Results and discussion

5.2.1 Synthesis of 2,3-diphenyl-1-vinyl-1*H*-phosphirene

Reported in 1995 by Deschamps and Mathey,¹ a new approach to 1-chlorophosphirenes **182** is certainly one of the most general and versatile methods for making these species. In line with this work, we decided to investigate the reaction of 1-chlorophosphirenes **183** with vinyl-Grignard reagents. Due to the high polarity of the $P(\delta^+)-Cl(\delta^-)$ bond, the vinyl-Grignard reagent easily attacks at the electrophilic phosphorus. We started our experiment by following the known procedure as shown in Scheme 5.1.²

Scheme 5.1

The reaction of AlCl_3 with 1- β -chloroethylphosphirene (**180**) led to 1-chlorophosphirene tungsten complex **181**. Next step, the displacement of $\text{W}(\text{CO})_5$ complex with 1,2-bis(diphenylphosphino)ethane (DPPE) at 80 °C for 1 h yielded 1-chlorophosphirene **182**. Without evaporation of solvent, 1.5 equiv. of vinyl magnesium bromide was then added to the reaction mixture at -78 °C and stirred at this temperature for 1 h and the 1-vinylphosphirene **183** was obtained in good yield.

To investigate the reactivity and the possibility of rearrangement of 1-vinylphosphirene **183** to form 4,5-diphenyl-3*H*-phosphole (**184**). The proposed rearrangement step is shown in Scheme 5.2.³

Scheme 5.2

Much attention has been devoted to the study of this reaction conditions as shown in Table 5.1. Unfortunately, we could not obtain the expected products. The above-mentioned reaction conditions have failed due to the low stability of phosphirene. They always led to complex mixtures of compounds because the decomposition of **183**. More research is yet to be done under various reaction conditions to promote the rearrangement of phosphirene to form phosphole.

Table 5.1 The reaction of 1-vinylphosphirene **183** under various conditions.

Entry	Solvent	Conditions	Results
1	toluene	150 °C, 1 h	decomposition of 183
2	toluene	reflux, 3 h	decomposition of 183
3	toluene	130 °C, 15 h	decomposition of 183
4	toluene	160 °C, 15 h	decomposition of 183
5	toluene	130 °C, 2 h	decomposition of 183
6	cyclohexane	UV, 3 h	decomposition of 183
7	methanol	UV, 3 h	decomposition of 183

5.2.2 Chemistry of 1,2,3-triphenylphosphirene sulfide

1,2,3-Triphenylphosphirene was described as the first stable tervalent phosphirene in 1984. Several approaches have been used to synthesize this tervalent phosphirene but the simplest method to prepare this compound is shown in Scheme 5.3. The reaction of PhPCl_2 and AlCl_3 with diphenylacetylene was carried out in CH_2Cl_2 at 25 °C for 30 min to generate the phosphirenium salt **185**, which appears to be rather unstable. The next step involves the treatment of the phosphirenium salt thus obtained with Bu_3P at 0 °C for 15 h to afford the expected 1,2,3-triphenylphosphirene **3** in moderate yield.⁴

Scheme 5.3

Another approach leading to the 1,2,3-triphenylphosphirene **3** using the decomplexation technique⁵ is provided in Scheme 5.4. It starts from the reaction of 1,2,3-triphenylphosphirene $P-W(CO)_5$ with iodine, which leads to the elimination of 1 CO and replacement by I_2 . After the disappearance of starting material peak on ^{31}P NMR, *N*-methylimidazole is then added at 25 °C and stirred for 20 h. The corresponding phosphirene **3** was obtained in 70% yield.

Scheme 5.4

From **3**, it is easy to get the corresponding phosphirene sulfide **37**. The discovery of phosphirene sulfide **37** was reported for the first time in 1984 but its chemistry was not investigated.^{5,6} **37** appears to be very unstable in solution. We first synthesized this phosphirene sulfide by following the same procedure and we were able to get **37** in 70% yield. However, all attempts to perform the purification of this compound and its X-ray crystal structure analysis failed due to its low stability (Scheme 5.5).

So we decided to move on for further reactions without any purification, by treatment of the phosphirene sulfide **37** with several trapping reagents. With 2,3-dimethyl-1,3-butadiene, in boiling toluene for 3 h, we observed a ^{31}P NMR signal at +65.2 ppm and according to the ^1H NMR spectrum, it corresponds to the six-membered heterocyclic compound **187**.⁷

Scheme 5.5

This chemistry is reminiscent of what was described in the literature⁷ with benz-phosphanorbornadiene sulfide Scheme 5.6.

Scheme 5.6

In the presence of MeOH, the phosphirene sulfide, thus generated in situ from the 1,2,3-triphenylphosphirene under the same conditions as described above gives the two isomers **194a** and **194b** (ratio = 91:9) that were isolated in 11% yield. The major isomer appears at higher field with a ^{31}P NMR signal at +86.3 ppm, while the other one appears at +98.7 ppm (Scheme 5.7).

Scheme 5.7

5.2.3 Chemistry of 1,2,3-triphenylphosphirene molybdenum complex

The initial synthesis of 1,2,3-triphenylphosphirene molybdenum complex (**189**) relied on a three-step scheme starting from phosphole **130** (Schemes 5.8-5.9). In a first step, the complexation of phosphole with molybdenum carbonyl at $0\text{ }^\circ\text{C}$ for 15 h, followed by cycloaddition of the phosphole complex **195** thus obtained with dimethyl acetylenedicarboxylate in hot toluene to give the phosphanorbornadiene molybdenum complex **196**.⁸

Scheme 5.8

Next step, the phosphanorbornadiene complex **196** thus formed decomposes to give the phosphinidene complex, which was trapped by diphenylacetylene leading to the expected 1,2,3-triphenylphosphirene molybdenum complex **197** in 21% yield.

Scheme 5.9

Thus, we have 1,2,3-triphenylphosphirene molybdenum complex (**197**) in hand. Next step is for checking whether the reaction of this complex with sulfur gives the same results as free 1,2,3-triphenylphosphirene does. A well-documented method for removing molybdenum from $[P-Mo(CO)_5]$ complexes is by sulfurization.⁷ So if we use this method to remove $Mo(CO)_5$ from **197**, then sulfurization using 2 equiv. of S_8 , we could get the phosphirene sulfide. To our surprise, we were unable to get the expected product. We observed various peaks on ^{31}P NMR spectroscopy, which cannot be separated.

In order to better understand the reasons for this failure in our case, we decided to add a trapping reagent such as 2,3-dimethyl-1,3-butadiene to the reaction mixture (Scheme 5.10). The reaction was performed in the presence of 2 equiv. of S_8 in boiling toluene. The progress of this reaction was monitored by ^{31}P NMR, the presence of a new peak at +38.7 ppm and the absence of the starting material peak indicated the completion of the reaction. The final product **198** was obtained in 52% yield. We found that the product is different from the 1,2,3-triphenylphosphirene case, whatever the amount of sulfur, we always obtain the product **198**.

Scheme 5.10

To determine whether the reaction of 1,2,3-triphenylphosphirene molybdenum complex also gives the same results as does free 1,2,3-triphenylphosphirene, we performed the reaction of phosphirene complex **197** with MeOH in the presence of sulfur and *N*-methylimidazole. Indeed, we could not obtain the expected product. We observed only one peak on the ^{31}P NMR at +32.5 ppm, which fits methyl phosphinate **199** (Scheme 5.11).⁹ Without sulfur this reaction did not proceed, only starting material was observed. The plausible reaction mechanism of **199** starts by the decomplexation of molybdenum from **197** to give the free phosphirene which then reacts with sulfur to give phosphirene sulfide **37**. Then, MeOH opens the ring and water in MeOH hydrolyzes P=S at 100 °C to give **199**.

Scheme 5.11

5.2.4 Chemistry of 1,2,3-triphenylphosphirene tungsten complex

The synthesis of 1,2,3-triphenylphosphirene tungsten complex has been reported in 1982 but the reactivity of this complex toward sulfur has not been described so far.¹⁰ We were interested in the reaction of 1,2,3-triphenylphosphirene tungsten complex (**5**) with sulfur in the presence of *N*-methylimidazole as a catalyst (Scheme 5.12). During the reaction, we observed the ^{31}P NMR signal change from

–166.2 ppm to –188.0 ppm, which corresponds to the decomplexation yielding 1,2,3-triphenylphosphirene. Then, the reaction was continued until the disappearance of the peak at –188.0 ppm and the peak at +21.2 ppm appeared. This reaction was completed in 2 days. After removal of the solvent and purification, unfortunately, the product **200** shows a ^{31}P NMR signal at +21.2 ppm, and disappears after column chromatography.

Scheme 5.12

The trapping reagent, 2,3-dimethyl-1,3-butadiene, was then added to this reaction (Scheme 5.13). We observed the cycloaddition product **201** in 38% yield.^{11,12} The plausible reaction mechanism of **201** starts by the decomplexation of tungsten from **6** to give the free phosphirene which then reacts with sulfur to give phosphirene sulfide **37**. The dissociation of **37**, followed by the trapping of $[\text{PhP}=\text{S}]$ with 2,3-dimethyl-1,3-butadiene gives **201** in 38% yield.

Scheme 5.13

5.3 Conclusion

Even though these various results cannot yet form the basis of a logical story at the moment, we plan to continue our experiments to rationalize the phosphirene-sulfide chemistry. We have the feeling that it can lead to the discovery of new aspects of phosphinidene chemistry.

5.4 Experimental

General Information:

NMR spectra were obtained on Bruker AV 500, BBFO1, BBFO2 or JEOL ECA400 and ECA 400SL spectrometer. All spectra were recorded at 298K. The chemical shift is given as dimensionless δ values and is frequency referenced relative to tetramethylsilane for ^1H and ^{13}C NMR spectroscopy. The ^{31}P NMR and ^{13}C NMR report as proton decoupled NMR spectra. In ^{13}C NMR spectra, the descriptors *cis* and *trans* (CO) refer to the position of carbonyl groups with respect to P. The Elemental Analysis Laboratory of the Division of Chemistry and Biological Chemistry at Nanyang Technological University of Singapore performed elemental analyses. HRMS spectra were obtained in ESI mode on a Finnigan MAT95XP HRMS system (Thermo Electron Corp.). X-ray crystallographic analyses were performed on a Bruker X8 APEX diffractometer. All reactions were performed using standard schlenk techniques under argon. Silica gel (230-400 mesh) was used for the chromatographic purifications. All the commercially available chemicals were used without prior drying or purification.

5.4.1 The synthesis of 1-chloro-2,3-diphenylphosphirene (**181**)

181

To 1- β -chloroethylphosphirene (**180**) (0.697 g, 1.17 mmol) in reaction flask, dry CH_2Cl_2 was added. Then, AlCl_3 (0.171 g, 1.28 mmol) was added portion wise at room temperature and stirred for 1.5 h. Saturated NH_4Cl was added to quench the reaction. Extraction by using CH_2Cl_2 and wash the organic layer with H_2O and sat. NaCl . Then dry organic layer by using MgSO_4 and evaporated. The residue was

chromatographed with 100% hexane to give **181** as a green solid (0.326 g, 49% yield).

^{31}P NMR (162 MHz, CDCl_3): δ -109.6 (s, $^1J_{\text{PW}} = 327.0$ Hz).

5.4.2 1-Chloro-2,3-diphenylphosphirene (**182**)

A solution of 1-chloro-2,3-diphenylphosphirene (0.176 g, 0.31 mmol) in 5 mL of toluene was stirred with DPPE (92.8 mg, 0.23 mmol) at 80 °C for 90 min. The reaction mixture was used for next step without purification. ^{31}P NMR (162 MHz, CDCl_3): δ -60.7 (s).

5.4.3 2,3-Diphenyl-1-vinyl-1*H*-phosphirene (**183**)

The reaction mixture of **182** was cooled to -78 °C, then vinyl magnesium bromide (0.47 mL, 0.47 mmol) was added dropwise and continue the reaction for 1 h. After evaporation of toluene, hexane was added to the residue and filtered off the solid. Removal of the solvent then purification by using hexane/ethyl acetate (90:10) to afford **183** (29.3 mg, 40% yield). ^{31}P NMR (162 MHz, CDCl_3): δ -185.8 ($^2J_{\text{PH}} = 32.3$ Hz, $^3J_{\text{PH}} = 15.0, 5.0$ Hz). ^1H NMR (400 MHz, CDCl_3): δ 7.86 (d, $J = 8.0$ Hz, 4H, ArH), 7.59-7.50 (m, 4H, ArH), 7.45-7.41 (m, 2H, ArH), 6.02 (dd, $J = 17.9, 1.8$ Hz, 1H, CHH), 5.92-5.83 (m, 1H, CH), 5.62 (ddd, $J = 32.7, 11.6, 1.8$ Hz, 1H, CHH). ^{13}C NMR (100 MHz, CDCl_3): δ 146.5 (d, $J = 63.0$ Hz, CH), 131.6 (C), 130.5 (2×CH), 130.0 (d, $J = 8.0$ Hz, C), 129.2 (2×CH), 128.9 (6×CH), 128.4 (C), 128.1 (d, $J = 29.0$

Hz, CH₂), 123.7 (d, $J = 42.0$ Hz, C). Exact mass: calcd for C₁₆H₁₃P 236.0755, found: 236.0761.

5.4.4 Synthesis of 1,2,3-triphenylphosphirene (**3**)

*Method A:*⁴

A solution of diphenylacetylene (2.00 g, 11.22 mmol) in 5 mL of CH₂Cl₂ was then slowly added to a solution of PhPCl₂ (1.50 mL, 11.05 mmol) and AlCl₃ (2.00 g, 15.00 mmol) in 10 mL of CH₂Cl₂ at room temperature under vigorous stirring. After 30 min, the dark green solution was transferred into a solution of Bu₃P (3.30 mL, 13.38 mmol) in 5 mL of CH₂Cl₂ at 0 °C within 5 min. The phosphirene **3** was isolated after chromatography on silica gel with hexane/CH₂Cl₂ (80:20) to give a blue solid (0.890 g, 28 % yield). ³¹P NMR (162 MHz, CDCl₃): δ −190.3 (s).

*Method B:*⁵

To a solution of phosphirene **6** (0.490 g, 0.80 mmol) in 5 mL of CH₂Cl₂, Iodine (0.200 g, 0.80 mmol) was added at 0 °C and stirred for 30 min. *N*-methylimidazole (0.07 mL, 1.60 mmol) was then added to a solution and stirred at room temperature for 15 h. After evaporation of the solvent the residue was chromatographed on silica gel by using 100% hexane to give **3** (0.161 g, 70% yield). ³¹P NMR (162 MHz, CDCl₃): δ −190.3 (s).

5.4.5 Synthesis of 1,2,3-triphenylphosphirene sulfide (**37**)

1,2,3-Triphenylphosphirene (0.773 g, 2.70 mmol), sulfur (71.8 mg, 2.80 mmol), and *N*-methylimidazole (0.15 mL) were stirred in CH_2Cl_2 at room temperature for 3 h. Hexane was added to the mixture and the solvent partially evaporated. The phosphirene sulfide **37** was obtained, after cooling of the mixture as a solid (0.450 g, 52% yield). ^{31}P NMR (162 MHz, CDCl_3): δ -77.0 (s).

5.4.6 Synthesis of **187**

187

A mixture of 1,2,3-triphenylphosphirene **3** (50.0 mg, 0.18 mmol), sulfur (5.6 mg, 0.18 mmol), *N*-methylimidazole (0.010 mL), and 2,3-dimethyl-1,3-butadiene (0.022 mL, 0.193 mmol) were carried out in 3 mL of toluene at 100 °C for 3 h. After evaporation of the solvent the residue was chromatographed on silica gel by using 100% hexane to give **187** (31.2 mg, 70% yield). ^{31}P NMR (162 MHz, CDCl_3): δ +65.2 (s). ^1H NMR (400 MHz, CDCl_3): δ 7.89-7.83 (m, 2H, *ArH*), 7.46-7.34 (m, 3H, *ArH*), 3.59 (t, J = 15.1 Hz, 1H, *CHH*), 3.27 (dd, J = 14.3 Hz, 1H, *CHH*), 2.93-2.87 (m, 2H, *CH*₂), 1.83 (d, J = 4.9 Hz, 3H, *CH*₃), 1.47 (s, 3H, *CH*₃). Exact mass: calcd for $\text{C}_{12}\text{H}_{15}\text{PS}_2$ 254.0353, found: 254.0350.

5.4.7 Synthesis of phosphine sulfide **194ab**

194ab

A mixture of 1,2,3-triphenylphosphirene **3** (50.0 mg, 0.175 mmol), sulfur (5.6 mg, 0.175 mmol), *N*-methylimidazole (0.010 mL), and MeOH (0.50 mL) were carried out in 3 mL of toluene at 100 °C for 3 h. After evaporation of the solvent the residue was chromatographed on silica gel by using 100% hexane to give **194ab** (7.0 mg, 11% yield). ^{31}P NMR (162 MHz, CDCl_3): δ +98.7 (s, major isomer) and +86.3 (s, minor isomer). ^1H NMR (400 MHz, CDCl_3) of major isomer and minor isomer: δ 7.82 (d, J = 25.5 Hz, 1H, CH), 7.68-7.62 (m, 2H, ArH), 7.47-7.43 (m, 1H, ArH), 7.37-7.32 (m, 2H, ArH), 7.28-7.21 (m, 3H, ArH), 7.17 (d, J = 7.1 Hz, 1H, ArH), 7.12 (t, J = 7.0 Hz, 2H, ArH), 7.01 (d, J = 7.4 Hz, 2H, ArH), 6.90 (dd, J = 6.3, 1.3 Hz, 2 Hz, ArH), 3.84 (d, J = 15.0 Hz, 3H, OCH_3 of minor isomer), 3.74 (d, J = 13.6 Hz, 3H, OCH_3 of major isomer). ^{13}C NMR (100 MHz, CDCl_3): δ 143.1 (d, J = 15.5 Hz, CH), 136.4 (d, J = 99.5 Hz, C), 135.1 (d, J = 8.3 Hz, C), 134.7 (d, J = 20.7 Hz, C), 132.9 (C), 131.9 (CH), 131.8 (2×CH), 130.4 (2×CH), 130.0 (CH), 129.9 (CH), 129.1 (CH), 128.6 (CH), 128.5 (CH), 128.2 (2×CH), 128.1 (CH), 128.0 (CH), 127.8 (CH), 51.6 (d, J = 5.9 Hz, OCH_3). Exact mass: calcd for $\text{C}_{21}\text{H}_{19}\text{OPS}$ 350.0894 found: 350.0899.

5.4.8 Preparation of 1-phenylphosphole molybdenum complex (**195**)

195

To a stirred suspension of molybdenum carbonyl (7.70 g, 29.3 mmol) in 20 mL CH_3CN , was added $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$ (3.25 g, 29.3 mmol) in small portions during 30 min. The yellow solution was stirred for further 30 min and evaporated to dryness under vacuum. The crude $\text{Mo(CO)}_5(\text{CH}_3\text{CN})$ thus obtained was dissolved in dry THF 20 mL. Phosphole **130** (5.00 g, 26.6 mmol) was added to a solution at 0 °C and stirred for 15 h. After evaporation, the residue was chromatographed on silica gel with 100%

hexane as eluent and later hexane/ethyl acetate (50:50) to give pale yellow product **195** (5.30 g, 47% yield). ^{31}P NMR (162 MHz, CDCl_3): δ +31.7 (s). ^1H NMR (400 MHz, CDCl_3): δ 7.51-7.45 (m, 2H, ArH), 7.37-7.34 (m, 3H, ArH), 6.52 (d, J = 37.6 Hz, 2H, 2 $\times$ CH), 2.12 (s, 6H, 2 $\times$ CH₃).

5.4.9 Preparation of 1-phenylphosphanorbornadiene molybdenum complex

(196)

196

Next step, 1-phenyl-3,4-dimethylphosphole molybdenum complex (**195**) (4.00 g, 9.43 mmol) was dissolved in 5 mL of toluene and dimethylacetylene dicarboxylate (4.63 mL, 37.7 mmol) was added dropwise. The mixture was heated at 70 °C for 2 days. After evaporation, the residue was chromatographed on silica gel with 100% hexane and then hexane/ethyl acetate (80:20) to give a yellow solid **196** (2.50 g, 47% yield). ^{31}P NMR (162 MHz, CDCl_3): δ + 239.0 (s).

5.4.10 Synthesis of phosphirene **197**

197

The 7-phosphanorbornadiene complex **196** (1.55 g, 2.74 mmol) and diphenylacetylene (0.730 g, 4.11 mmol) in 25 mL of toluene was heated at 120 °C for 15 h. After evaporation of the solvent the residue was chromatographed on silica gel by using 100% hexane to give **197** (0.300 g, 21% yield). ^{31}P NMR (162 MHz, CDCl_3):

δ -138.0 (s). ^1H NMR (400 MHz, CDCl_3): δ 7.92-7.91 (m, 3H, ArH), 7.58-7.47 (m, 9H, ArH), 7.40-7.31 (m, 3H, ArH).

5.4.11 Synthesis of **198**

198

A mixture of 1,2,3-triphenylphosphirene molybdenum complex (**197**) (50.1 mg, 0.096 mmol), sulfur (3.0 mg, 0.096 mmol), and 2,3-dimethyl-1,3-butadiene (0.012 mL, 0.101 mmol) were carried out in 1 mL of toluene at 100 °C for 3 h. After evaporation of the solvent the residue was chromatographed on silica gel by using 100% hexane to give **198** (23.0 mg, 52% yield). ^{31}P NMR (162 MHz, CDCl_3): δ +38.7 (s). ^1H NMR (400 MHz, CDCl_3): δ 7.60-7.55 (m, 2H, ArH), 7.46-7.36 (m, 3H, ArH), 3.14 (dd, J = 7.4 Hz, 1H, CHH), 3.04-2.98 (m, 2H, CH_2), 2.83 (d, J = 16.0 Hz, CHH), 1.69 (s, 3H, CH_3), 1.54 (s, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3): δ 210.2 (d, J = 24.7 Hz, *trans* CO), 205.1 (d, J = 10.6 Hz, *cis* CO), 136.8 (d, J = 20.7 Hz, C), 129.7 (CH), 129.6 (C), 129.6 (CH), 128.4 (CH), 128.3 (CH), 127.1 (d, J = 10.4 Hz, C), 125.5 (d, J = 9.7 Hz, C), 37.9 (d, J = 13.0 Hz, CH_2), 32.5 (d, J = 2.5 Hz, CH_2), 21.5 (d, J = 4.8 Hz, CH_3), 19.6 (CH_3). Exact mass: calcd for $\text{C}_{17}\text{H}_{15}\text{O}_5\text{PSMo}$ 459.9432, found: 459.9433.

5.4.12 Synthesis of **199**

199

A mixture of 1,2,3-triphenylphosphirene molybdenum complex (**197**) (50.1 mg, 0.096 mmol), sulfur (3.0 mg, 0.096 mmol), and MeOH (0.5 mL) were carried out

in 1 mL of toluene at 110 °C for 15 h. After evaporation of the solvent the residue was chromatographed on silica gel by using hexane/ethyl acetate (50:50) to give **199** (5.0 mg, 16% yield). ^{31}P NMR (162 MHz, CDCl_3): δ +32.4 (s). ^1H NMR (400 MHz, CDCl_3): δ 7.70 (d, J = 22.0 Hz, 1H, *CH*), 7.60-7.55 (m, 2H, *ArH*), 7.49-7.46 (m, 1H, *ArH*), 7.38-7.33 (m, 2H, *ArH*), 7.29-7.23 (m, 3H, *ArH*), 7.17 (d, J = 7.1 Hz, 1H, *ArH*), 7.12 (t, J = 7.0 Hz, 2H, *ArH*), 7.03 (d, J = 7.3 Hz, 2H, *ArH*), 6.98 (m, 2H, *ArH*), 3.78 (d, J = 11.1 Hz, 3H, OCH_3). ^{13}C NMR (100 MHz, CDCl_3): δ 143.1 (d, J = 10.2 Hz, CH), 135.5 (d, J = 9.1 Hz, C), 134.7 (d, J = 19.2 Hz, C), 133.3 (C), 132.2 (CH), 132.1 (2×CH), 130.4 (2×CH), 129.6 (CH), 129.5 (CH), 129.0 (CH), 128.7 (2×CH), 128.3 (CH), 128.2 (2×CH), 128.1 (CH), 127.7 (CH), 51.4 (OCH_3). Exact mass: calcd for $\text{C}_{21}\text{H}_{19}\text{O}_2\text{P}$ 334.1123, found: 334.1121.

5.4.13 Synthesis of **201**

201

A mixture of 1,2,3-triphenylphosphirene tungsten complex (**6**) (50.0 mg, 0.082 mmol), sulfur (2.65 mg, 0.082 mmol), *N*-methylimidazole (0.002 mL), and 2,3-dimethyl-1,3-butadiene (0.019 mL, 0.164 mmol) were carried out in 3 mL of toluene at 100 °C for 3 h. After evaporation of the solvent the residue was chromatographed on silica gel by using hexane/ CH_2Cl_2 (80:20) to give **201** (7.0 mg, 38% yield). ^{31}P NMR (162 MHz, CDCl_3): δ +45.7 (s). ^1H NMR (400 MHz, CDCl_3): δ 7.90-7.85 (m, 2H, *ArH*), 7.54-7.45 (m, 3H, *ArH*), 3.07 (d, J = 9.6 Hz, 4H, 2× CH_2), 1.80 (s, 3H, 2× CH_3). Exact mass: calcd for $\text{C}_{12}\text{H}_{15}\text{PS}$ 222.0632, found: 222.0636.

5.5 References

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APPENDIX

Table A1 Crystallographic Data for compound **134** **134**

Empirical formula	C ₂₂ H ₁₉ O ₅ P Si W
Formula weight	606.28
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)
Unit cell dimensions	
$a = 9.5783(3)$ Å	$\alpha = 90^\circ$.
$b = 9.7533(3)$ Å	$\beta = 90.589(2)^\circ$.
$c = 12.4712(4)$ Å	$\gamma = 90^\circ$.
Volume	1165.00(6) Å ³
Z	2
Density (calculated)	1.728 Mg/m ³
Absorption coefficient	5.107 mm ⁻¹
F(000)	588
Crystal size	0.30 x 0.20 x 0.06 mm ³
Theta range for data collection	2.67 to 35.73°.
Index ranges	-15 ≤ h ≤ 15, -16 ≤ k ≤ 15, -20 ≤ l ≤ 20
Reflections collected	30398
Independent reflections	10244 [R(int) = 0.0335]
Completeness to theta = 35.73°	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7492 and 0.3095
Refinement method	Full-matrix-block least-squares on F ²
Data / restraints / parameters	10244 / 429 / 548
Goodness-of-fit on F ²	1.065
Final R indices [I > 2σ(I)]	R1 = 0.0196, wR2 = 0.0386
R indices (all data)	R1 = 0.0260, wR2 = 0.0410
Absolute structure parameter	0.21(3)
Largest diff. peak and hole	1.507 and -1.116 e.Å ⁻³

Table A2 Crystallographic Data for compound **151** **151**

Empirical formula	C ₂₅ H ₂₄ N O ₅ P W
Formula weight	633.27
Temperature	113(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	
$a = 16.2834(3)$ Å	$\alpha = 90^\circ$.
$b = 9.3069(2)$ Å	$\beta = 110.1880(10)^\circ$.
$c = 17.4048(3)$ Å	$\gamma = 90^\circ$.
Volume	2475.62(8) Å ³
Z	4
Density (calculated)	1.699 Mg/m ³
Absorption coefficient	4.766 mm ⁻¹
F(000)	1240
Crystal size	0.12 x 0.10 x 0.06 mm ³
Theta range for data collection	1.48 to 34.35°.
Index ranges	-25 ≤ h ≤ 25, -14 ≤ k ≤ 14, -27 ≤ l ≤ 24
Reflections collected	52987
Independent reflections	10236 [R(int) = 0.0593]
Completeness to theta = 34.35°	98.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7630 and 0.5986
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	10236 / 0 / 302
Goodness-of-fit on F ²	1.098
Final R indices [I > 2σ(I)]	R1 = 0.0323, wR2 = 0.0712
R indices (all data)	R1 = 0.0581, wR2 = 0.0916
Largest diff. peak and hole	1.727 and -2.154 e.Å ⁻³

Table A3 Crystallographic Data for compound **155** **155**

Empirical formula	C ₂₆ H ₂₅ N O ₁₀ P ₂ W ₂
Formula weight	941.11
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	
a = 13.2742(4) Å	α = 90°.
b = 12.2704(4) Å	β = 108.164(2)°.
c = 20.1250(6) Å	γ = 90°.
Volume	3114.61(17) Å ³
Z	4
Density (calculated)	2.007 Mg/m ³
Absorption coefficient	7.536 mm ⁻¹
F(000)	1784
Crystal size	0.40 x 0.20 x 0.20 mm ³
Theta range for data collection	1.63 to 37.00°.
Index ranges	-19 ≤ h ≤ 22, -20 ≤ k ≤ 20, -34 ≤ l ≤ 23
Reflections collected	92462
Independent reflections	15624 [R(int) = 0.0319]
Completeness to theta = 37.00°	98.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.3141 and 0.1525
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	15624 / 115 / 436
Goodness-of-fit on F ²	1.190
Final R indices [I > 2σ(I)]	R1 = 0.0262, wR2 = 0.0677
R indices (all data)	R1 = 0.0442, wR2 = 0.0888
Largest diff. peak and hole	1.416 and -1.504 e.Å ⁻³

Table A4 Crystallographic Data for compound **158** **158**

Empirical formula	C ₃₄ H ₄₄ N ₂ O ₄
Formula weight	544.71
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	Cc
Unit cell dimensions	
a = 22.0421(6) Å	α = 90°.
b = 11.3051(3) Å	β = 126.3530(10)°.
c = 15.4125(7) Å	γ = 90°.
Volume	3093.15(18) Å ³
Z	4
Density (calculated)	1.170 Mg/m ³
Absorption coefficient	0.076 mm ⁻¹
F(000)	1176
Crystal size	0.14 x 0.12 x 0.10 mm ³
Theta range for data collection	2.14 to 25.24°.
Index ranges	-22 ≤ h ≤ 26, -13 ≤ k ≤ 13, -18 ≤ l ≤ 18
Reflections collected	12283
Independent reflections	4910 [R(int) = 0.0366]
Completeness to theta = 25.24°	98.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9924 and 0.9894
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4910 / 2 / 371
Goodness-of-fit on F ²	1.129
Final R indices [I > 2σ(I)]	R1 = 0.0434, wR2 = 0.1129
R indices (all data)	R1 = 0.0587, wR2 = 0.1385
Largest diff. peak and hole	0.427 and -0.281 e.Å ⁻³

Table A5 Crystallographic Data for compound **170** **170**

Empirical formula	C37.50 H20.50 B Cl1.50 F15 N O6 P W
Formula weight	1144.85
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	
$a = 11.2518(5)$ Å	$\alpha = 77.600(2)^\circ$
$b = 11.4277(5)$ Å	$\beta = 78.274(2)^\circ$
$c = 16.4537(8)$ Å	$\gamma = 72.811(2)^\circ$
Volume	$1951.73(15)$ Å ³
Z	2
Density (calculated)	1.948 Mg/m ³
Absorption coefficient	3.224 mm ⁻¹
F(000)	1110
Crystal size	$0.28 \times 0.10 \times 0.04$ mm ³
Theta range for data collection	1.89 to 37.69°
Index ranges	$-19 \leq h \leq 17$, $-19 \leq k \leq 19$, $-28 \leq l \leq 28$
Reflections collected	55516
Independent reflections	20390 [R(int) = 0.0412]
Completeness to $\theta = 37.69^\circ$	97.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8819 and 0.4655
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	20390 / 30 / 599
Goodness-of-fit on F ²	1.063
Final R indices [I > 2sigma(I)]	R1 = 0.0357, wR2 = 0.0799
R indices (all data)	R1 = 0.0488, wR2 = 0.0935
Largest diff. peak and hole	1.912 and -1.736 e.Å ⁻³

Table A6 Crystallographic Data for compound **174** **174**

Empirical formula	C ₂₅ H ₂₄ N O ₅ P W
Formula weight	633.27
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	
$a = 16.1263(3)$ Å	$\alpha = 90^\circ$.
$b = 9.4786(2)$ Å	$\beta = 127.4470(10)^\circ$.
$c = 20.0072(3)$ Å	$\gamma = 90^\circ$.
Volume	2427.95(8) Å ³
Z	4
Density (calculated)	1.732 Mg/m ³
Absorption coefficient	4.859 mm ⁻¹
F(000)	1240
Crystal size	0.40 x 0.36 x 0.30 mm ³
Theta range for data collection	3.35 to 43.48°.
Index ranges	-30 ≤ h ≤ 31, -18 ≤ k ≤ 17, -38 ≤ l ≤ 38
Reflections collected	64898
Independent reflections	18315 [R(int) = 0.0376]
Completeness to theta = 43.48°	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.3235 and 0.2467
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	18315 / 0 / 302
Goodness-of-fit on F ²	1.006
Final R indices [I > 2sigma(I)]	R1 = 0.0252, wR2 = 0.0503
R indices (all data)	R1 = 0.0440, wR2 = 0.0556
Largest diff. peak and hole	2.642 and -1.576 e.Å ⁻³

Table A7 Crystallographic Data for compound **179ab** **179ab**

Empirical formula	C37 H28 B F15 N O6 P W
Formula weight	1093.23
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	
$a = 10.8060(4)$ Å	$\alpha = 69.386(2)^\circ$
$b = 13.2637(5)$ Å	$\beta = 87.030(2)^\circ$
$c = 15.0392(5)$ Å	$\gamma = 82.802(2)^\circ$
Volume	2001.55(12) Å ³
Z	2
Density (calculated)	1.814 Mg/m ³
Absorption coefficient	3.042 mm ⁻¹
F(000)	1068
Crystal size	0.40 x 0.30 x 0.10 mm ³
Theta range for data collection	1.45 to 30.50°
Index ranges	-15 ≤ h ≤ 15, -18 ≤ k ≤ 18, -21 ≤ l ≤ 21
Reflections collected	49578
Independent reflections	12095 [R(int) = 0.0433]
Completeness to theta = 30.50°	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7507 and 0.3758
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	12095 / 1027 / 1014
Goodness-of-fit on F ²	1.068
Final R indices [I > 2σ(I)]	R1 = 0.0459, wR2 = 0.1123
R indices (all data)	R1 = 0.0689, wR2 = 0.1311
Largest diff. peak and hole	2.521 and -2.529 e.Å ⁻³