NEW ASPECTS OF PHOSPHIRENE CHEMISTRY

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Duanghathai Panichakul
13 April 2012
LIST OF PUBLICATIONS


TABLE OF CONTENTS

Acknowledgments i
List of publications ii
Abstract vi
List of tables vii
List of symbols and abbreviations viii
Chapter 1: Introduction to phosphirene chemistry 1
  1.1) Overview 1
  1.2) Structural data of phosphirenes 2
  1.3) Spectroscopic data of phosphirenes 7
  1.4) Aromaticity 8
  1.5) Reactivity of phosphirenes 12
    1.5.1) Reactions at phosphorus of the ring 12
    1.5.2) Reactions at ring carbon 17
    1.5.3) Reactions with cleavage of one P–C bond of the ring 18
    1.5.4) Reactions with cleavage of two P–C bonds of the ring 22
    1.5.5) Ring expansions 22
  1.6) Synthesis 25
    1.6.1) From P and C$_2$ units 25
    1.6.2) From PC and C units 28
    1.6.3) By cyclisation of C–P–C units 30
  1.7) References 31
Chapter 2: New route to functionalized phosphirenes: reactivity of 2-silyl- and 2-stannyl-substituted phosphirenes

2.1) Overview

2.2) Introduction

2.3) Results and discussion

2.4) Conclusion

2.5) Experimental

2.6) References

Chapter 3: Special chemistry of 2-aminophosphirenes: synthesis, structure, and chemistry of 2-amino-substituted phosphirenes

3.1) Overview

3.2) Introduction

3.3) Results and discussion

3.4) Conclusion

3.5) Experimental

3.6) References

Chapter 4: Special chemistry of 2-aminophosphirenes: serendipitous discovery of a phosphirene-phosphindole rearrangement

4.1) Overview

4.2) Introduction

4.3) Results and discussion

4.4) Conclusion
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 °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 [PdL₂] 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 PhCCN'Pr₂ with terminal phosphinidene complexes [R−PW(CO)₅], generated from phosphanorbornadiene complex, affords the corresponding phosphirenes (R = Ph, OMe) and the diphosphetene (R = 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.
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>The structural data of phosphirene derivatives</td>
<td>2-4</td>
</tr>
<tr>
<td>1.2</td>
<td>NMR data for some selected phosphirenes</td>
<td>7-8</td>
</tr>
<tr>
<td>2.1</td>
<td>Selected bond lengths (Å) and angles (°) for 2-silylphosphirene 134</td>
<td>38</td>
</tr>
<tr>
<td>3.1</td>
<td>Selected bond lengths (Å) and angles (°) for 2-aminophosphirene 151</td>
<td>63</td>
</tr>
<tr>
<td>3.2</td>
<td>Selected bond lengths (Å) and angles (°) for the diphosphetene 155</td>
<td>65</td>
</tr>
<tr>
<td>3.3</td>
<td>Selected bond lengths (Å) and angles (°) for arene 158</td>
<td>68</td>
</tr>
<tr>
<td>4.1</td>
<td>Selected bond lengths (Å) and angles (°) for 170</td>
<td>82</td>
</tr>
<tr>
<td>4.2</td>
<td>Selected bond lengths (Å) and angles (°) for phosphindole 174</td>
<td>85</td>
</tr>
<tr>
<td>4.3</td>
<td>Significant distances (Å) and angles (°) for 176</td>
<td>86</td>
</tr>
<tr>
<td>4.4</td>
<td>Selected bond lengths (Å) and angles (°) for phosphine complex 179a</td>
<td>89</td>
</tr>
<tr>
<td>5.1</td>
<td>The reaction of 1-vinylphosphirene 183 under various conditions</td>
<td>102</td>
</tr>
</tbody>
</table>
# LIST OF SYMBOLS AND ABBREVIATIONS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tr>
<td>Alk</td>
<td>Alkyl group</td>
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<tr>
<td>Ar</td>
<td>Aryl group</td>
</tr>
<tr>
<td>br</td>
<td>broad</td>
</tr>
<tr>
<td>Bu</td>
<td>Butyl group</td>
</tr>
<tr>
<td>calcd</td>
<td>calculated</td>
</tr>
<tr>
<td>CDCl$_3$</td>
<td>chloroform-d$_1$</td>
</tr>
<tr>
<td>CD$_2$Cl$_2$</td>
<td>methylene chloride-d$_2$</td>
</tr>
<tr>
<td>Cp</td>
<td>cyclopentadienyl</td>
</tr>
<tr>
<td>d</td>
<td>doublet (in NMR assignments)</td>
</tr>
<tr>
<td>DPPE</td>
<td>1,2-bis(diphenylphosphino)ethane</td>
</tr>
<tr>
<td>dd</td>
<td>doublet of doublet (in NMR assignments)</td>
</tr>
<tr>
<td>equiv.</td>
<td>equivalent</td>
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<td>Et</td>
<td>Ethyl group</td>
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<tr>
<td>g</td>
<td>grams</td>
</tr>
<tr>
<td>h</td>
<td>hour(s)</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Hex</td>
<td>Hexyl group</td>
</tr>
<tr>
<td>HCl</td>
<td>hydrochloric acid</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>HRMS</td>
<td>high resolution mass spectroscopy</td>
</tr>
<tr>
<td>(J)</td>
<td>coupling constant (in NMR assignments)</td>
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<tr>
<td>(^3)Pr</td>
<td>isopropyl group</td>
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<tr>
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<td>multiplets (in NMR assignments)</td>
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<td>Me</td>
<td>methyl</td>
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<td>mg</td>
<td>milligram(s)</td>
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<td>MS</td>
<td>mass spectroscopy</td>
</tr>
<tr>
<td>Nu</td>
<td>nucleophile</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>OTf</td>
<td>triflate group</td>
</tr>
<tr>
<td>Ph</td>
<td>Phenyl</td>
</tr>
<tr>
<td>(^{31})P NMR</td>
<td>(^{31})P(^{1}H) NMR</td>
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</tbody>
</table>
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. 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. Synthesis of free tervalent 1H-phosphirene (3) was then reported by Marinetti, Mathey, Fischer, and Mitschler in 1984. 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 Regitz discovered the first stable 2H-phosphirene 4 from the reaction of phosphaalkyne with diazo cyclohexane.

![Figure 1.1](image-url)

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 $47^\circ$ to $51^\circ$. The lengths of $P\text{--}C$ bond are between 1.780 to 1.890 Å and the $C\text{--}C$ 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.

<table>
<thead>
<tr>
<th>Phosphirenes</th>
<th>Bond angles (°)</th>
<th>Bond lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C\text{--}P\text{--}C$</td>
<td>$C\text{--}P\text{--}R$</td>
</tr>
<tr>
<td>Ph$_3$P=Cl$_2$</td>
<td>42.8</td>
<td>106.6</td>
</tr>
<tr>
<td>Ph$_3$P=Cl$_2$ (OC)$_3$W</td>
<td>108.6</td>
<td>68.7</td>
</tr>
<tr>
<td>Ph$_3$P=Cl$_2$</td>
<td>41.8</td>
<td>104.0</td>
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<tr>
<td>Ph$_3$P=Cl$_2$</td>
<td>104.4</td>
<td>1.821</td>
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Table 1.1 (cont.) The structural data of phosphirene derivatives.

<table>
<thead>
<tr>
<th>Phosphirenes</th>
<th>Bond angles (°)</th>
<th>Bond lengths (Å)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>C−P−C</td>
<td>C−P−R</td>
</tr>
<tr>
<td>(OC)₅W₄Bu</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>49.2</td>
<td>56.7</td>
</tr>
<tr>
<td>(OC)₅W₄Ph</td>
<td>50.7</td>
<td>44.7</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>128.7</td>
</tr>
<tr>
<td>(OC)₅W₄Ph</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>44.0</td>
<td>109.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>111.7</td>
</tr>
<tr>
<td>(OC)₅W₄Ph</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>46.1</td>
<td>66.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>67.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>43.5</td>
<td>68.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>43.1</td>
<td>107.91</td>
</tr>
<tr>
<td></td>
<td></td>
<td>109.11</td>
</tr>
</tbody>
</table>
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.
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. 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. 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 Regitz 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 free and complexed phosphaalkenes, 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 phosphaalkene. In the mean time, Tran Huy, Fischer, and Mathey obtained the X-ray crystal structure of a metallaphosphirene 7. 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. 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 pyramidality 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 phosphirenenium salt \(^7\) \(^9\) 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 complex \(^9\) \(^11\) 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 complex \(^10\) \(^12\) 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 units \(^11\), gives similar results as phosphirene complex \(^5\). In 2005, a structure of the first bicyclic phosphirene, 2-aza-1-phoshabicyclo-[5.1.0]oct-7-ene \(^14\) was confirmed by X-ray analysis \(^12\). 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 complex \(^13\) \(^15\) 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 complex\textsuperscript{14} 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

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

Table 1.2 NMR data for some selected phosphirenes.

<table>
<thead>
<tr>
<th>Phosphirenes</th>
<th>\textsuperscript{31}P</th>
<th>\textsuperscript{13}C</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>–190.3</td>
<td>122.7 (\textsuperscript{1}J_{CP} = 43.9 Hz, =C–P)</td>
</tr>
<tr>
<td>6</td>
<td>–161.4</td>
<td>130.2 (\textsuperscript{1}J_{CP} = 24.0 Hz, =C–P)</td>
</tr>
</tbody>
</table>
δ, ppm using 85% H$_3$PO$_4$ 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)π], 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$_3$H$_3^{+}$) was Breslow in late 1950.\textsuperscript{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

<table>
<thead>
<tr>
<th>Phosphirenes</th>
<th>$^{31}$P</th>
<th>$^{13}$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph[Ph]P(OC)$_3$W[Cl]</td>
<td>-109.7</td>
<td>143.2 ($^1J_{CP} = 22.0$ Hz, $=$C–P)</td>
</tr>
<tr>
<td>Ph[Ph]P(OC)$_3$Mo[F]</td>
<td>-16.7</td>
<td>149.4 ($^1J_{CP} = 19.0$ Hz, $=$C–P)</td>
</tr>
<tr>
<td>Ph[Ph]P[Bu]\(\otimes) B(OTf)$_4$</td>
<td>+309.7</td>
<td>215.4 ($^1J_{CP} = 94.9$ Hz, $=$C–$^-$Bu)</td>
</tr>
<tr>
<td>+19.0 Hz, $=$C–Ph)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Et[Et]P[W(CO)$_5$](\otimes)B(OTf)$_4$</td>
<td>+232.6</td>
<td>197.2 ($^1J_{CP} = 40.5$ Hz, C=C)</td>
</tr>
</tbody>
</table>
are far from being solved. Here are some examples of phosphirene derivatives. The structure of phosphirenylum 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.

![Phosphirene Derivatives](image)

**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 Mathey\textsuperscript{20} investigated the synthesis of 1-chlorophosphirenes 17 in the coordination sphere of tungsten by treatment of AlCl\textsubscript{3} with 1-β-chlorophosphirene 27. They proposed the phosphirenylum cation 29 as an intermediate from the loss of ethylene group in the transient cation 28, followed by treatment with sat. NH\textsubscript{4}Cl to generate 17 (Scheme 1.1).
Scheme 1.1

A few years later, the same authors\textsuperscript{21} demonstrated that bis(phosphirenyl) oxide 30 can give a stable complex at oxygen with AlCl\textsubscript{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 Regitz\textsuperscript{17} reported the first successful generation of persistent phosphirenylium cation 19 from the reaction of phosphirene 34 with B(OSO\textsubscript{2}CF\textsubscript{3})\textsubscript{3} in liquid SO\textsubscript{2} at \(-78 \, ^\circ\text{C}\) under argon. The phosphirenylium cation shows a very characteristic peak of \(\textsuperscript{31}\text{P} \text{NMR}\) very downfield at \(\delta +309.7 \, \text{ppm}\). Due to very low stability, this cation must be kept in liquid SO\textsubscript{2} at below \(-40 \, ^\circ\text{C}\). It must be noted that
this reaction requires an extremely strong Lewis acid B(OSO₂CF₃)₃ to bond with trifluoromethane sulfonate ion leading to B(OSO₂CF₃)₄⁻.

![Scheme 1.3](image)

**Scheme 1.3**

At the same time, Nixon et al.²² described the synthesis and characterization of the first compounds containing a stable η⁶-phosphirenyl cation in a red-orange nickel complex 35. This complex was synthesized by condensation of phosphaalkyne ('BuC≡P) with nickel atoms at 77K. The ³¹P signal of the phosphirenyl ring shows relatively high field position at −161.0 ppm.

![Scheme 1.4](image)

**Scheme 1.4**

In 1999, Laali and Regitz¹⁸ demonstrated that the phosphirenylium 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 SO₂ at −55 °C generated phosphirenylium complex 20. The ³¹P NMR spectra of 20 shows a dramatic shift to +232.6 ppm with a huge J(P-W) coupling at 392.8 Hz when compared to starting phosphirene complex δ −35.4 ppm, J(P-W) 343.8 Hz. The large coupling constant of this phosphirenylium complex indicates that this phosphirenylium cation is coordinated to pentacarbonyl tungsten by η¹-coordination (Scheme 1.5).
From these results, it is clear that the phosphirenylium ion does exist but for an
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).²³ᵃᵇ

The reaction of a powerful alkylation agent such as trimethyloxonium
tetrafluoroborate with triphenylphosphirene (3) in CH₂Cl₂ at room temperature
produces a phosphireniun salt 38 (Scheme 1.7).²³ᵃ
Similarly, bromination of 1,2,3-triphenylphosphirene (3) in the presence of AlCl$_3$ also gives a bromo phosphireniun salt 39 (Scheme 1.8).$^{23b}$

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-$\beta$-chloroethylphosphirene to give chlorophosphirene 17. The driving force for this reaction is the aromaticity of 29 (Scheme 1.9).$^{15}$

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).$^{21}$
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

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 Na$_2$Fe(CO)$_4$, free chlorophosphirene 47 can transform to the dimeric structure 54 as shown in Scheme 1.16.$^2^5$

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).$^{1^4}$
Scheme 1.17

The condensation 1-alkynylphosphirene 57 with terminal phosphinidene unit [PhCCP–W(CO)₅], generated from 1-alkynylphosphanorbornadiene complex, gave biphosphirene complex 58. The next step shows the reaction of biphosphirene 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 'BuLi, followed by trapping with acetone (Scheme 1.19).²⁷
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).\textsuperscript{23a}

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 phosphireniendum salts 38 leads to the ring-opened product 64 (Scheme 1.21).\textsuperscript{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).\textsuperscript{23a}

Scheme 1.23

According to the high electrophilicity of 1,2,3-triphenylphosphirene, it is not surprising that \textit{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).\textsuperscript{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).

\[
\text{Ph}_2\text{C}=\text{P} + 2 \left[ \text{Na}^+ \right] \rightarrow \text{Ph}_2\text{C}=\text{P}^- + 2 \text{Na}^+ \\
\text{THF} \quad -70^\circ \text{C}, 10 \text{ min}
\]

\[
\begin{align*}
\text{1) CH}_3\text{I} \\
\text{2) H}^+ \\
\text{3) S}_8
\end{align*}
\]

\[
\begin{align*}
\text{Ph}_2\text{C}=\text{P} \quad &+ \quad \text{Ph}_2\text{C}=\text{P}^- \\
\text{Ph}_2\text{P} \quad &+ \quad \text{Ph}_2\text{P}
\end{align*}
\]

\[
\begin{align*}
\text{73} \\
\text{74}
\end{align*}
\]

Scheme 1.25

Following the results mentioned above, it was found that \textit{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 \textit{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).
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

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 \(-78 \, ^\circ\text{C}\) 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 °C in the
presence of carbon monoxide pressure can easily insert CO into phosphirene units
providing 88 (Scheme 1.30). 31

\[
\text{Scheme 1.30}
\]

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

\[
\text{Scheme 1.31}
\]

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

\[
\text{Scheme 1.32}
\]
In addition, the insertion of alkynes into one of the phosphorus-carbon bonds of phosphirene complex 93 in the presence of Pd(PPh$_3$)$_4$ yields phosphole complexes 94 (Scheme 1.33).  

![Scheme 1.33](image)

Also possible is the insertion of terminal phosphinidene units into the conjugatively destabilized P–C$_2$ bond of 2-alkynylphosphirene 95 leads to diphosphetene complex 96 with cis-stereochemistry (Scheme 1.34).  

![Scheme 1.34](image)

In the same vein, [PtCl$_2$(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).  

![Scheme 1.35](image)
Scheme 1.36 shows another example for ring expansion of phosphirenes. Under thermal conditions, intramolecular reorganization of 1-allylphosphirenes provides bicyclic phosphiranes.37

![Scheme 1.36](image)

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 (Scheme 1.37).38

![Scheme 1.37](image)

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 phosphanorbomadiene complexes,103 generated from cycloaddition of phospholes with dimethyl acetylene dicarboxylate (Scheme 1.38).

15
More recently, Lammertsma and co-workers reported a new access to phosphinidene complexes from benzophosphepine complexes 107, generated from homologation-oxidation of commercially available α-phthalaldehyde 105 to give 1,2-diethynylbenzene 106 then hydrophosphination with the complexed phosphine yielding benzophosphepine complexes 107 (Scheme 1.39). 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 tervalent phosphirenes 3 (Scheme 1.40). 1,15
Besides, aminophosphirenes 108 can be synthesized from transient aminophosphinidene complex 86 with alkynes (Scheme 1.41). 37b

\[
\begin{align*}
(\text{Et}_2\text{N})_2\text{P} - \text{H} & \quad \text{W(CO)}_5 \\
\text{Ph} & \quad = \quad = \quad \text{R} \\
\text{Br}_3, \alpha\text{-picoline} & \quad 25 \degree \text{C} \\
\text{86} & \quad \text{108}
\end{align*}
\]

\( R = \text{Ph, H} \)

Scheme 1.41

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

\[
\begin{align*}
\text{R}^\prime - \text{P} = \text{N} & \quad \text{R}' \\
+ \quad \text{R}'' - \equiv - \equiv & \quad \text{R}'' \\
\text{109} & \quad \text{110}
\end{align*}
\]

\( R = \text{Me, Et, PhCH}=\text{CH}, \text{Cl}; R' = 2,4,6-\text{tBuC}_6\text{H}_2 \)

\( R = \text{Et}_3\text{C}; R' = \text{tBu} \)

\( R'' = \text{Ph, COOMe} \)

Scheme 1.42

One of the simplest methods for the synthesis of phosphirenes starts from dichlorophosphines, AlCl₃, and alkynes at room temperature in dichloromethane to give chlorophosphireniurn salts 111. Reduction of these salts using tributylphosphine affords the expected tervalent phosphirenes 112 (Scheme 1.43). 41a,b

\[
\begin{align*}
\text{RPCl}_2 & \quad + \quad \text{AlCl}_3 \\
& \quad + \quad \text{R}' - \equiv - \equiv \text{R}'' \\
& \quad \text{CH}_2\text{Cl}_2, 25 \degree \text{C} \\
\text{111} & \quad \text{112}
\end{align*}
\]

\( R = \text{Me, Et, Ph, 'Bu, Me}_2\text{N, Mes} \)

\( R', R'' = \text{H, Me, Et, Ph} \)

Scheme 1.43
Another approach to synthesize phosphirenes from a P and C₂ unit uses titanacycloprenes 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](image)

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

![Scheme 1.45](image)

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 phosphaalkynes or phosphaalkenes with carbene sources. A siloxy-substituted phosphaalkene 118 reacts with silyl carbenoid to give an unusual phosphirene 119 (Scheme 1.46). 44
Similarly, condensation of a stable phosphinocarbene with phosphaalkyne yields $2H$-phosphirene 120 (Scheme 1.47). \(^{45}\)

\[
\begin{align*}
R_2PCSiMe_3 + \text{Bu}^-\text{C≡P} & \xrightarrow{-30 \, ^\circ \text{C}} R_2P\text{SiMe}_3\text{Bu}^- \\
R = \text{NPr}_2
\end{align*}
\]

Scheme 1.47

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

\[
\begin{align*}
R^-\text{C≡P} + \text{N} = \text{N} & \xrightarrow{\Delta} R\text{P} \text{Cl} \text{R}' \\
R = \text{'Bu}, 1\text{-Ad}, \text{CMe}_2\text{Et} \\
R' = \text{'Bu}, \text{Ph}, \text{CH}_2\text{Ph}, \text{MeO}, \text{EtO}, \text{PhO}
\end{align*}
\]

Scheme 1.48

A similar chemistry has been found later using 1,2-dichlorocyclopropenes 122 (Scheme 1.49). \(^{47}\)
Finally, the reaction of a chlorocarbene precursor and a silyl-substituted phosphaalkene 125 provided chlorophosphirene 121 (Scheme 1.50). 46

\[
\begin{align*}
\begin{array}{c}
\text{Cl} \equiv \text{P} \equiv \text{SiMe}_3 \\
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{R} \end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{125} \\
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\Delta
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{R} \equiv \text{P} \equiv \text{SiMe}_3 \\
\text{R}' \equiv \text{N} \equiv \text{N} \equiv \text{Cl}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{126} \\
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{130 °C} \\
\text{neat}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{R} \equiv \text{P} \equiv \text{R} \\
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{121} \\
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{R} = \text{Ph, SiMe}_3 \\
\text{R}' = \text{Ph, Pho}
\end{array}
\end{align*}
\]

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

\[
\begin{align*}
\begin{array}{c}
\text{Ar} \equiv \text{P} \equiv \text{SiMe}_3 \\
\text{SiMe}_3
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{Cl} \equiv \text{Cl}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{THF, –78 °C}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{127}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{Ar} \equiv \text{P} \equiv \text{SiMe}_3 \\
\text{SiMe}_3
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{Cl} \equiv \text{Li}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{THF, –78 °C}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{128}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{Me}_3\text{Si}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{129}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{Ar} = 2,4,6-\text{Bu}_3\text{C}_6\text{H}_2
\end{array}
\end{align*}
\]

Scheme 1.51
1.7 References


23. (a) Marinetti, A.; Mathey, F. *J. Am. Chem. Soc.* 1985, 107, 4700. (b) Marinetti,
45.
1253.
28. Vanderark, L. A.; Clark, T. J.; Rivard, E.; Manners, I.; Sloot, J. C.;


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 °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 [PdL₂] as a catalyst leads to an alkynylphosphine by [1,3] migration of tin from C to P.

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](image)

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\textsuperscript{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](image)

Scheme 2.2

Upon heating, the generated [PhP–W(CO)]\textsubscript{5} 133 from 7-phosphanorbornadiene precursor 132 was treated with PhCCSiMe\textsubscript{3} to give the expected 2-silylphosphirene 134 in 87% yield (Scheme 2.3).

![Scheme 2.3](image)

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.

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Bond angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(1)–C(6)</td>
<td>1.884(5)</td>
</tr>
<tr>
<td>C(6)–C(7)</td>
<td>1.319(5)</td>
</tr>
<tr>
<td>C(6)–P(1)</td>
<td>1.812(4)</td>
</tr>
<tr>
<td>C(7)–C(8)</td>
<td>1.446(9)</td>
</tr>
<tr>
<td>C(7)–P(1)</td>
<td>1.791(5)</td>
</tr>
<tr>
<td>C(17)–P(1)</td>
<td>1.819(2)</td>
</tr>
<tr>
<td>C(7)–C(6)–P(1)</td>
<td>67.7</td>
</tr>
<tr>
<td>C(7)–C(6)–Si(1)</td>
<td>148.7</td>
</tr>
<tr>
<td>P(1)–C(6)–Si(1)</td>
<td>143.5</td>
</tr>
<tr>
<td>C(6)–C(7)–C(8)</td>
<td>148.5</td>
</tr>
<tr>
<td>C(6)–C(7)–P(1)</td>
<td>69.4</td>
</tr>
<tr>
<td>C(8)–C(7)–P(1)</td>
<td>142.2</td>
</tr>
</tbody>
</table>

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 (SiMe₃, W(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 W(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 °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](image)

**Scheme 2.4**

Phosphirene 135 is characterized by the expected high-field shift of its $^{31}$P resonance at δ −156.6 ppm in CD$_2$Cl$_2$ and its highly deshielded vinylic proton at +8.48 ppm with a $^2J_{HP}$ coupling of 21.0 Hz. Phosphirene 136 exists as a 1:1 mixture of two nonseparable diastereomers with their phosphorus resonances at high fields (δ $^{31}$P −149.5 and −149.3 ppm in CD$_2$Cl$_2$). 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 (δ $^{31}$P +197.2 ppm in CDCl$_3$), its huge $^1J_{FP}$ coupling of 850.0 Hz,
and its $^{19}\text{F}$ 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](image)

The hydrolysis product 138 shows the two expected vinylic carbons at 142.9 (=CHPh, $^2J_{CP} = 9.6$ Hz) and 129.0 ppm (=CHP, $^1J_{CP} = 34.5$ Hz). The CHPh proton shows a $^3J_{PH}$ coupling of 18.0 Hz, in agreement with an $E$ geometry. 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 ($^2J_{CP} = 14.4$ 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, $\text{F}^-$ 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](image)

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 PhCCSnBu₃ 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 [PdL₂] catalyst (Scheme 2.8). Secondary phosphine 141 displays a \(^{31}\text{P}\) resonance at −59.9 ppm (CDCl₃) with a \(^1J_{HP}\) coupling at 372.5 Hz. Its \(^{13}\text{C}\) spectrum shows the two sp carbons at 109.2 \((^{2}J_{CP} = 13.4 \text{ Hz})\) and 78.5 ppm \((^{1}J_{CP} = 82.4 \text{ Hz})\). It appears that [PdL₂] readily catalyzes the [1,3] shift of tin from carbon to phosphorus. This is not a real surprise since it is known that 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)_3] 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 product 142 even with the reaction at room temperature for 1 h (Scheme 2.10).

![Scheme 2.10](image_url)

We described the synthesis of 2-silylphosphirene 134 from the reaction of [PhP=W(CO)_3] and PhCCSiMe_3. By continuing this research, we decided to perform the reaction of phosphanorbornadiene complex 132, as a precursor of [PhP=W(CO)_3], with Me_3Si(CC)SiMe_3 in boiling toluene. Whatever ratios of phosphanorbornadiene complex 132 and Me_3Si(CC)SiMe_3, 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 δ^{31}P = -146.3 ppm in CDCl_3 with J_{PW} = 280.5 Hz.
The next attempted approach to functionalize the phosphirene ring was to use PhCCSO₂Ph 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 PhCCS(O)₂Tol 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 PhCCSO₂Ph 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 ³¹P resonance at high fields (δ ³¹P = -108.8 ppm in CDCl₃ with ¹J_PW = 280.5 Hz).

However, when we tried the reaction of 2-sulfonylphosphirene with various metallic reagents, for example vinyl magnesium bromide, isopropyl magnesium bromide, n-BuLi, or MeLi at −78 °C in THF, we were unable to detect the expected phosphirene products. We only observed complex mixtures on ³¹P 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 $^1$H 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)\textsuperscript{3a}

\[
\begin{array}{c}
\text{Me} \\
\text{Me}
\end{array}
\]

\[
\text{(OC)}_5\text{W} \overset{\text{Ph}}{\text{P}}
\]

131

To a stirred suspension of tungsten carbonyl (10.55 g, 30.0 mmol) in 20 mL CH\textsubscript{3}CN, was added Me\textsubscript{3}NO\textsubscript{2}H\textsubscript{2}O (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\textsubscript{5})(CH\textsubscript{3}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 131 (10.5 g, 77% yield). \textsuperscript{31}P NMR (162 MHz, CDCl\textsubscript{3}): \( \delta +10.6 \) (s, \( ^1J_{PW} = 214.7 \) Hz).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta 7.49-7.36 \) (m, 5H, ArH), 6.47 (d, \( ^2J_{PH} = 37.1 \) Hz, 2H, 2×CH\textsubscript{2}), 2.18 (s, 6H, 2×CH\textsubscript{3}). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \( \delta 199.1 \) (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−CH\textsubscript{3}), 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 (CH\textsubscript{3}), 17.3 (CH\textsubscript{3}).

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

\[
\begin{array}{c}
\text{Me} \\
\text{Me}
\end{array}
\]

\[
\text{(OC)}_5\text{W} \overset{\text{Ph}}{\text{P}} \overset{\text{CO\textsubscript{2}Me}}{\text{CO\textsubscript{2}Me}}
\]

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$_3$): $\delta$ +208.8 (s, $^1J_{PW}$ = 236.6 Hz). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.36-7.14 (m, 5H, Ar$H$), 3.97 (s, 2H, $2\times$CH$\ell$), 3.64 (s, 6H, $2\times$OCH$_3$), 2.03 (s, 6H, $2\times$CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 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, =C(CO$_2$Me)), 141.2 (=C(CO$_2$Me)), 141.1 (=C(CH$_3$)), 140.3 (=C(CH$_3$)), 138.0 (d, $J = 16.2$ Hz, ipso C), 130.1 (CH), 129.8 ($2\times$CH), 129.5 ($2\times$PCH), 128.3 (d, $J = 29.6$ Hz, $2\times$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

![Diagram](image)

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$_3$): $\delta$ –177.5 (s, $^1J_{PW}$ = 273.6 Hz). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.75 (d, $J = 6.9$ Hz, 2H, Ar$H$), 7.55-7.48 (m, 3H, Ar$H$), 7.40-7.32 (m, 5H, Ar$H$), 0.38 (s, 9H, $3\times$CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 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, =C(Ph)), 139.1 (d, $J = 11.5$ Hz, ipso C(PhP)), 131.7 (d, $J = 35.5$ Hz, =C–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 ($2\times$CH(PhP)), 128.5 (CH), 128.4 (CH), 127.6 (d, $J = 7.7$ Hz, ipso C(PhC)), –0.70 ($3\times$CH$_3$). The $^{13}$C
assignments were made by comparison with previous data.\textsuperscript{8} Ana. Calcd for
C\textsubscript{22}H\textsubscript{19}O\textsubscript{2}PSiW: 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)

\[
\begin{array}{c}
\text{Ph} \\
\downarrow \\
\text{P} \\
\downarrow \\
\text{Ph}
\end{array}
\quad CH(OH)Ph
\quad (\text{OC})_5\text{W}
\]

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-\textit{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: \textsuperscript{31}P NMR (162 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \( \delta = -149.5 \) and \( -149.3 \) (d, \( J_{PW} = 269.0, 282.0 \) Hz). \textsuperscript{1}H NMR (400 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \( \delta = 7.78-7.76 \) (m, 2H, \textit{Ar}H, minor isomer), \( 7.73-7.70 \) (m, 2H, \textit{Ar}H, major isomer), \( 7.52-7.47 \) (m, 12H, \textit{Ar}H, mixture of two isomers), \( 7.42-7.35 \) (m, 4H, \textit{Ar}H, mixture of two isomers), \( 7.33-7.23 \) (m, 10H, \textit{Ar}H), \( 6.25 \) (d, \( J = 2.8 \) Hz, 1H, \( CH–Ph \)), \( 6.18 \) (d, \( J = 5.0 \) Hz, 1H, \( CH–Ph \)), 2.68 (br s, 2H, 2\textsuperscript{\times }OH). \textsuperscript{13}C NMR (100 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \( \delta = 198.6 \) and \( 198.5 \) (2d, \( J = 29.6, 30.5 \) Hz, \textit{trans} CO), \( 196.7 \) and \( 196.6 \) (2d, \( J = 18.1 \) Hz, \textit{cis} CO), \( 140.5 \) (d, \( J = 8.6 \) Hz, =C(Ph)), \( 138.9 \) (2d, \( J = 5.7, 8.6 \) Hz, =C(Ph)), \( 133.9 \) (2d, \( J = 13.4 \) Hz, \textit{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,
2.5.4.2 1,3-Diphenylphosphirene (135)

\[
\begin{array}{c}
\text{Ph} \\
\text{(OC)}_3\text{W} \\
\text{Ph}
\end{array}
\]

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). \(^{31}\)P NMR (162 MHz, CDCl\(_3\)): \(\delta\) –156.6 (s, \(^{1}J_{PW} = 273.6\) Hz). \(^{1}\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 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). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 198.2 (d, \(J = 31.5\) Hz, \text{trans CO}), 196.2 (td, \(J = 62.0, 8.6\) Hz, \text{cis CO}), 138.29 and 138.27 (dd, \(J = 9.6\) Hz, \(=C\text{Ph + ipso PhP}\)), 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 C\(_{19}\)H\(_{17}\)O\(_5\)PW: 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)

\[ \text{Ph} \quad \text{(OC)}_3 \text{W} \quad \text{Ph} \quad \text{H} \quad \text{H} \quad \text{P} \quad \text{F} \]

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$_3$): $\delta$ +197.2 (dd, $^1J_{PF}$ = 850.1 Hz, $^1J_{PW}$ = 324.3 Hz) and +201.8 (dd, $^1J_{PF}$ = 850.1 Hz, $^1J_{PW}$ = 324.3 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$, PhCF$_3$): –132.8 (d, $^1J_{PF}$ = 839.7 Hz).

2.5.5.2 Alkenylphosphinous acid (138)

\[ \text{Ph} \quad \text{(OC)}_3 \text{W} \quad \text{Ph} \quad \text{H} \quad \text{P} \quad \text{OH} \]

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$_2$Cl$_2$): $\delta$ +101.6 (s, $^1J_{PW}$ = 280.5 Hz). $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ 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, =CHPh), 6.84 (dd, $J$ =
22.9, 17.4 Hz, 1H, =CHP), 4.00 (br s, 1H, OH). 13C NMR (100 MHz, CD2Cl2): 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×CH), 128.9 (CH), 128.8 (CH), 128.7 (CH), 128.7 (CH), 127.6 (2×CH). Anal. Calcd for C19H13O6PW: 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

\[
\begin{align*}
\text{Ph} & \equiv \text{H} \\
\text{H} & \text{P} - \text{OMe} \\
\text{(OC)}_3\text{W} & \text{Ph}
\end{align*}
\]

139a

31P NMR (162 MHz, CDCl3): δ +117.6 (s, 1J_PW = 284.8 Hz). 1H NMR (400 MHz, CDCl3): 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, OCH3). 13C NMR (100 MHz, CDCl3): 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×CH), 129.0 (CH), 128.9 (CH), 127.9 (2×CH), 125.7 (d, J = 38.3 Hz, CH), 54.3 (d, J = 6.7 Hz, OCH3). Exact mass: Calcd. For C20H15O6PW: 566.0116. Found: 566.0106.
2.5.6.2 Alkenylphosphinite 139b

\[
\begin{array}{c}
\text{H} \\
\text{P} \\
\text{Ph} \\
\text{H} \\
(\text{OC})_3 \text{W} \\
\end{array}
\]

139b

\(^{31}\)P NMR (162 MHz, CDCl\(_3\)): \(\delta +125.9\) (s, \(^1J_{PW} = 284.8\) Hz). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.66-7.61 (m, 2H, Ar\(H\)), 7.50-7.44 (m, 3H, Ar\(H\)), 7.24-7.17 (m, 3H, Ar\(H\)), 7.08-7.06 (m, 2H, Ar\(H\)), 6.18 (d, \(J = 32.0\) Hz, 1H, =CH \textit{trans} P), 6.14 (d, \(J = 16.0\) Hz, 1H, =CH \textit{cis} P), 3.50 (d, \(J = 13.7\) Hz, 3H, OCH\(_3\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 198.8 (d, \(^1J_{PW} = 27.8\) Hz, \textit{trans} CO), 196.9 (td, \(J = 10.2, 7.7\) Hz, \textit{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 C\(_{20}\)H\(_{15}\)O\(_6\)PW: 566.0116, found 566.0109.

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

\[
\begin{array}{c}
\text{Ph} \\
\text{SnBu}_3 \\
\text{P} \\
(\text{OC})_3 \text{W} \\
\text{Ph} \\
\end{array}
\]

140

The 7-phphanorbonadiene 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\(_3\)): \(\delta -179.9\) (s, \(^1J_{PW} = 273.5\) Hz). \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 7.93 (d, \(J = 6.9\) Hz, 2H, Ar\(H\)), 7.65-7.54 (m, 5H, Ar\(H\)), 7.43 (br s, 3H, Ar\(H\)), 1.76-1.70 (m, 6H, 3\(\times\)CH\(_2\)), 1.50-1.41 (m, 12H, 3\(\times\)CH\(_2\)CH\(_2\)), 0.98 (t, \(J = 3.0\) Hz, 9H, 3\(\times\)CH\(_2\)).
3\times CH_3). ^{13}C NMR (100 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \delta 199.2 (d, \textit{J} = 30.6 Hz, \textit{trans} CO), 197.4 (d, \textit{J} = 8.6 Hz, \textit{cis} CO), 148.6 (d, \textit{J} = 14.4 Hz, C), 141.0 (d, \textit{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 CH), 130.0 (2\times CH), 129.0 (CH), 128.9 (CH), 29.9 (t, \textit{J} = 22.0 Hz, 3\times CH\textsubscript{2}), 28.1 (t, \textit{J} = 59.4 Hz, 3\times CH\textsubscript{2}), 14.2 (3\times CH\textsubscript{3}), 12.4 (3\times CH\textsubscript{2}). Anal. Calcd for C\textsubscript{31}H\textsubscript{37}O\textsubscript{5}P\textsubscript{Sn}W: C, 45.23; H, 4.53. Found: C, 45.62; H, 4.02.

2.5.8 Preparation of Alkynylphosphine 141

\[
\begin{array}{c}
\text{Ph} \\
\equiv \\
\text{P} \\
\text{W(CO)}\textsubscript{5}
\end{array}
\]

141

The catalyst was prepared from Pd(dba)\textsubscript{2} (16.4 mg, 0.03 mmol) and PPh\textsubscript{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\textsubscript{3}): \delta -59.9 (dd, ^{1}J_{PH} = 372.5 Hz, ^{1}J_{PW} = 236.7 Hz). ^{1}H NMR (400 MHz, CDCl\textsubscript{3}): \delta 7.76-7.71 (m, 2H, Ar\textit{H}), 7.57-7.49 (m, 5H, Ar\textit{H}), 7.42-7.38 (m, 3H, Ar\textit{H}), 6.48 (d, ^{1}J_{PH} = 372.0 Hz, 1H, PH). ^{13}C NMR (100 MHz, CDCl\textsubscript{3}): \delta 199.0 (d, \textit{J} = 23.0 Hz, \textit{trans} CO), 195.9 (d, \textit{J} = 6.7 Hz, \textit{cis} CO), 132.6 (2\times 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 CH), 128.0 (d, \textit{J} = 4.8 Hz, C), 109.2 (d, \textit{J} = 13.4 Hz, C), 78.5 (d, \textit{J} = 82.4 Hz, C). Exact mass: Calcd. For C\textsubscript{19}H\textsubscript{17}O\textsubscript{5}PW: 533.9853, found 533.9865.
2.5.9 Preparation of phenylphosphinous acid 142

\[
\text{Ph} \quad \overset{\text{HO-}^\text{P-}^\text{H}}{\text{W(CO)\textsubscript{5}}}
\]

142

The 7-phosphanorbornadiene 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). \(^{31}\text{P}\) NMR (162 MHz, CDCl\(_3\)): \(\delta +84.4\) (s, \(^1J_{\text{PW}} = 276.1\) Hz, \(^1J_{\text{PH}} = 359.3\) Hz). \(^1\text{H}\) NMR (400 MHz, CD\(_2\)Cl\(_2\)): \(\delta 8.27\) (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

\[
\text{Me}_3\text{Si} \quad \equiv \equiv \equiv \text{SiMe}_3
\]

144

The 7-phosphanorbornadiene complex 132 (0.600 g, 0.86 mmol) and Me\(_3\)Si(CC)\(_3\)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). \(^{31}\text{P}\) NMR (202 MHz, CDCl\(_3\)): \(\delta -146.9\) (s, \(^1J_{\text{PW}} = 280.5\) Hz). \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): \(\delta 7.41-7.34\) (m, 5H, ArH), 0.33 (s, 9H, SiMe\(_3\)), 0.25 (s, 9H, SiMe\(_3\)). \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)): \(\delta 197.5\) (d, \(J = 54.3\) Hz, \textit{trans CO}), 195.7 (d, \(J = 11.5\) Hz, \textit{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), \(-0.54\) (SiMe\(_3\)), \(-1.31\) (SiMe\(_3\)). Exact mass: calcd for C\(_{23}\)H\(_{23}\)O\(_5\)PSi\(_2\)W 650.0331, found: 650.0337.

### 2.5.11 Synthesis of phosphirene 145

![Structure of phosphirene 145](image)

The 7-phosphanorbornadiene complex 132 (0.131 g, 0.20 mmol) and PhCCSO\(_2\)Ph (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/CH\(_2\)Cl\(_2\) (50:50) to give phosphirene 145 (91.8 mg, 68% yield). \(^{31}\)P NMR (162 MHz, CDCl\(_3\)): \( \delta -108.9 \) (s, \( ^1J_{PW} = 280.5 \) Hz). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta 8.04\text{-}7.97 \) (m, 4H, ArH), 7.71\text{-}7.67 (m, 1H, ArH), 7.65\text{-}7.61 (m, 1H, ArH), 7.59\text{-}7.54 (m, 4H, ArH), 7.48\text{-}7.42 (m, 3H, ArH), 7.38\text{-}7.34 (m, 2H, ArH). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta 196.7 \) (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 C\(_{25}\)H\(_{15}\)O\(_5\)PSW 673.9785, found: 673.9790.
2.6 References


CHAPTER 3

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

3.1 Overview

The reaction of the bulky ynamine PhCCNPr$_2$ with terminal phosphinidene complexes [R−PW(CO)$_5$], generated from phosphanorbomadiene complex, affords the corresponding phosphirenes for R = Ph and OMe and the diphosphetene for R = Me. The structure of 1-phenylphosphirene shows elongated P−C(N) and C=C ring bonds. 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.


Panichakul, D.; Mathey, F. Presented at the PERCH-CIC Congress VII, 4-7 May 2011, Chonburi, Thailand.

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). 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.

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. However, it is known that pentavalent phosphirenes show a high propensity to ring-opening 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, based on the well-established generation of $[\text{PhP-W(CO)}_5]$ from phosphanorbornadiene complex 132, the reaction of $[\text{PhP-W(CO)}_5]$ 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).

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 PhCCNPr$_2$. A general procedure for the
synthesis of PhCCN\textsuperscript{i}Pr\textsubscript{2} is shown in Scheme 3.3.\textsuperscript{5,6} This reaction proceeds in two steps, first, the in situ formation of the 1,1-difluoro alkene \textsuperscript{149} from benzaldehyde, triphenylphosphine, and sodium chlorodifluoroacetate. Then, by reacting the alkene thus obtained with 2 equiv. of lithium diisopropylamine the ynamine \textsuperscript{150} (PhCCN\textsuperscript{i}Pr\textsubscript{2}) is obtained in good yield.

\[
\text{CICF}_2\text{COONa} + (\text{C}_6\text{H}_5)_3\text{P} + \text{PhCHO} \rightarrow \text{PhHC=CF}_2
\]

\textsuperscript{149}

2 LiN\textsuperscript{i}Pr\textsubscript{2}

\textsuperscript{150}

Scheme 3.3

We started our investigation by the reaction of [RP−W(CO)\textsubscript{5}] and PhCCN\textsuperscript{i}Pr\textsubscript{2} in boiling toluene. To our delight, the desired phosphirene complexes were obtained as shown in Scheme 3.4. When \( R = \text{Ph} \) and \( R = \text{OMe} \), the phosphirene products were produced in 54\% and 68\% yield, respectively.

\[
\begin{align*}
\text{(OC)}_3\text{W} & \quad \text{toluene} \quad 110 ^\circ \text{C} \\
\text{[RP-W(CO)\textsubscript{5}]} & \rightarrow \text{[RP-W(CO)\textsubscript{5}]} \\
\text{Ph\equiv=N\textsuperscript{i}Pr\textsubscript{2}} & \rightarrow \text{Ph\equiv=N\textsuperscript{i}Pr\textsubscript{2}} \\
\text{151} & \quad \text{R = Ph} \quad (54\%) \\
\text{152} & \quad \text{R = MeO} \quad (68\%)
\end{align*}
\]

Scheme 3.4

The presence of the three-membered ring phosphirenes in \textsuperscript{151} and \textsuperscript{152} is obvious from the \( ^{31}\text{P} \) chemical shifts at high fields: \textsuperscript{151}, \( \delta = -141.0 \) (\( ^1J_{pw} = 271.6 \text{ Hz} \)) and \textsuperscript{152}, \( \delta = -56.1 \) (\( ^1J_{pw} = 325.6 \text{ Hz} \)). Based on our previous results,\textsuperscript{7} the phosphirene complex generated from the methoxyphosphinidene unit and diphenylacetylene gives
$^{31}$P chemical shift at $\approx$61.4 ($^{1}J_{PW} = 266.0$ Hz). It should be noted that, there is a significant influence on the chemical shift, when replacing the phenyl by the NPr$_2$ substituent, but no marked difference in terms of the $^{1}J_{PW}$ 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 C=C(N) double bond, for example for 152: $\delta$ C(Ph) 102.6 (s), C(N) 141.5 (d, $^{1}J_{CP} = 22.9$ 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 (Å) and angles (°) are provided in Figure 3.1 and Table 3.1, respectively.

![Figure 3.1](image.png)

**Figure 3.1** X-ray crystal structure analysis of phosphirene 151.
Table 3.1 Selected bond lengths (Å) and angles (°) for 2-aminophosphirene 151.

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Bond angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(7)−N(1)</td>
<td>1.332(4)</td>
</tr>
<tr>
<td>C(7)−C(8)</td>
<td>1.343(4)</td>
</tr>
<tr>
<td>C(7)−P(1)</td>
<td>1.806(3)</td>
</tr>
<tr>
<td>C(8)−P(1)</td>
<td>1.768(3)</td>
</tr>
<tr>
<td>C(8)−C(9)</td>
<td>1.457(4)</td>
</tr>
<tr>
<td>C(15)−P(1)</td>
<td>1.833(3)</td>
</tr>
</tbody>
</table>

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 (ΣC−N−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 pentacarboxyltungsten complex (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]pentacarboxyl 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 20\textsuperscript{th} century, Averin et al.\textsuperscript{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 [MeP–W(CO)\textsubscript{5}] with PhCCN\textsubscript{iPr\textsubscript{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).

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.\textsuperscript{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.

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(1)–P(2)</td>
<td>2.2185(9)</td>
</tr>
<tr>
<td>P(1)–C(8)</td>
<td>1.872(3)</td>
</tr>
<tr>
<td>P(2)–C(1)</td>
<td>1.809(3)</td>
</tr>
<tr>
<td>C(1)–C(8)</td>
<td>1.381(4)</td>
</tr>
<tr>
<td>C(8)–N(1)</td>
<td>1.353(4)</td>
</tr>
<tr>
<td>P(1)–C(15)</td>
<td>1.835(3)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(1)–P(2)–C(1)</td>
</tr>
<tr>
<td>P(2)–P(1)–C(8)</td>
</tr>
<tr>
<td>P(1)–C(8)–C(1)</td>
</tr>
<tr>
<td>P(2)–C(1)–C(8)</td>
</tr>
<tr>
<td>C(15)–P(1)–P(2)–C(21)</td>
</tr>
<tr>
<td>C(1)–C(8)–P(1)–P(2)</td>
</tr>
</tbody>
</table>

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°. Moreover, the two Me–P substituents are in a \textit{trans} disposition. Based on the previous literature as shown in Scheme 3.6\textsuperscript{11,12}

![Scheme 3.6](image)

\textbf{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 \textit{trans} R–P–P–R product whereas, in the previous cases described in the literature, only or mainly the \textit{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 \([\text{MeP–Cr(CO)}_5] > [\text{PhP–Cr(CO)}_5] > [\text{MeOP–Cr(CO)}_3]\). 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.\(^\text{13}\) 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.\(^\text{1}\) 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](image-url)
Table 3.3 Selected bond lengths (Å) and angles (°) for arene 158.

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Dihedral angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)–C(2)</td>
<td>1.393(4)</td>
</tr>
<tr>
<td>C(2)–C(3)</td>
<td>1.389(4)</td>
</tr>
<tr>
<td>C(3)–C(4)</td>
<td>1.402(4)</td>
</tr>
<tr>
<td>C(4)–C(5)</td>
<td>1.423(4)</td>
</tr>
<tr>
<td>C(5)–C(6)</td>
<td>1.415(4)</td>
</tr>
<tr>
<td>C(6)–C(1)</td>
<td>1.395(4)</td>
</tr>
<tr>
<td>C(4)–N(1)</td>
<td>1.432(4)</td>
</tr>
<tr>
<td>C(6)–N(2)</td>
<td>1.421(4)</td>
</tr>
</tbody>
</table>

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. 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, $C$-CO$_2$Me), 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 $\beta$ 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 $\alpha$-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.
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-d4. 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 seperations. 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 ºC 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

![Phosphirene 151](image)
Yield: 35.0 mg, 54%. $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ −140.9 (s, $^1J_{PW} = 271.6$ Hz). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.55-7.48 (m, 4H, Ar$H$), 7.40-7.35 (m, 5H, Ar$H$), 7.25-7.21 (m, 1H, Ar$H$), 3.89 (sep, 2H, $2\times$CH), 1.32 (d, $J = 6.8$ Hz, 6H, $2\times$CH$_3$), 1.19 (d, $J = 6.8$ Hz, 6H, $2\times$CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 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(Ph)), 130.8 (s, meta CH(Ph)), 130.4 (d, $J = 10.6$ Hz, meta CH(PhP)), 130.0 (d, $J = 6.7$ Hz, ortho CH(PhP)), 128.2 (s, para CH(PhP)), 115.8 (s, =C(PhP)), 53.9 (2×CH), 24.5 (2×CH$_3$), 24.0 (2×CH$_3$). Anal. Calcd. for C$_{25}$H$_{24}$NO$_5$PW: C, 47.41; H, 3.82. Found: C, 47.62; H, 4.02.

3.5.1.2 Phosphirene 152

Yield: 40.0 mg, 68%. $^{31}$P NMR (162 MHz, CD$_2$Cl$_2$): $\delta$ −56.1 (s, $^1J_{PW} = 325.6$ Hz). $^1$H NMR (400 MHz, CD$_2$Cl$_2$, $-40$ °C): $\delta$ 7.44-7.37 (m, 4H, Ar$H$), 7.27-7.23 (t, $J = 7.1$ Hz, 1H, Ar$H$), 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, $2\times$CH$_3$), 1.26 (d, $J = 6.9$ Hz, 3H, CH$_3$). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$, $-60$ °C): $\delta$ 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 C$_{20}$H$_{22}$NO$_6$PW: C, 40.91; H, 3.78. Found: C, 40.25; H, 3.50.
3.5.1.3 Diphosphetene 155

\[
\begin{array}{c}
\text{Ph} \quad \text{N} \quad \text{Pr}_2 \\
\text{(OC)}_2 \text{W} - \text{P} - \text{P} \cdots \text{Me} \\
\text{Me} \quad \text{W}(\text{CO})_5
\end{array}
\]

155

Yield: 27.0 mg, 57%. \(^{31}\text{P}\) NMR (162 Hz, CDCl\(_3\)): \(\delta +28.0 \text{ (d, } {^1J_{PW}} = 230.0 \text{ Hz,}
{^1J_{PP}} = 8.7 \text{ Hz).} \)

\(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): \(\delta 7.36-7.30 \text{ (m, 3H, ArH), 7.9 \text{ (d, } J = 7.3 \text{ Hz, 2H, ArH), 3.90-3.83 \text{ (sep, 2H, 2×CH),}
2.38 \text{ (dd, } J = 17.8, 5.5 \text{ Hz, 3H, P–CH}_3\text{), 2.24 \text{ (dd, } J = 17.8, 5.5 \text{ Hz, 3H, P–CH}_3\text{), 1.24 \text{ (d, } J = 6.8 \text{ Hz, 6H, 2×CH}_3\text{), 1.19 \text{ (d, } J = 6.8 \text{ Hz, 6H, 2×CH}_3\text{).} \)

\(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)): \(\delta 198.2 \text{ (d, } J = 23.9 \text{ Hz, trans CO), 197.6 \text{ (d, } J = 23.9 \text{ Hz, trans CO), 196.1}
\text{ (d, } J = 5.7 \text{ Hz, cis CO), 195.9 \text{ (d, } J = 6.7 \text{ Hz, cis CO), 150.1 \text{ (dd, } J = 38.1, 22.9 \text{ Hz,}
=\text{C–N), 137.8 \text{ (dd, } J = 15.3, 8.6 \text{ Hz, ipso C(Ph)), 129.0 \text{ (2×CH), 128.9 \text{ (m, ortho and}
meta CH(Ph)), 128.3 \text{ (para CHPh), 116.1 \text{ (dd, } J = 42.0, 20.4 \text{ Hz, } =\text{C(Ph)), 52.2 \text{ (d, } J =
4.8 \text{ Hz, 2×CH), 26.8 \text{ (dd, } J = 10.5, 8.6 \text{ Hz, P–CH}_3\text{), 24.0-23.7 \text{ (m, P–CH}_3\text{, 2×CH}_3\text{),}
21.7 \text{ (2×CH}_3\text{).} \)

Anal. Caled. for C\(_{26}\)H\(_{25}\)NO\(_{10}\)P\(_2\)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

Yield: 6.2 mg, 24%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.32-7.27 (m, 10H, ArH), 3.75 (s, 3H, CO$_2$C$_3$H$_3$), 3.35 (s, 3H, CO$_2$C$_3$H$_3$), 3.16 (sep, 2H, 2\times CH), 3.00 (sep, 2H, 2\times CH), 0.79 (d, $J$ = 6.5 Hz, 6H, 2\times CH$_3$), 0.73 (d, $J$ = 6.5 Hz, 6H, 2\times CH$_3$), 0.56 (d, $J$ = 6.5 Hz, 6H, 2\times CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 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 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 CH), 50.3 (2\times CH), 22.6 (2\times CH$_3$), 22.3 (2\times CH$_3$), 21.9 (2\times CH$_3$), 21.8 (2\times CH$_3$).

3.5.2.2 Phosphole 159

Yield: 37.0 mg, 50%. $^{31}$P NMR (162 MHz, CD$_2$Cl$_2$): $\delta$ +24.5 (s, $^1J_{PW} = 245.4$ Hz). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_2$CH$_3$), 3.63 (s, 3H, CO$_2$CH$_3$), 3.49-3.42 (sep, 2H, 2\times CH), 1.16 (d, $J$ = 6.6 Hz, 6H, 2\times CH$_3$), 1.00 (d, $J$ = 6.6 Hz, 6H, 2\times CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 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, $\alpha$-COO), 161.8 (d, $J = 11.5$ Hz, $\beta$-COO), 157.5 (d, $J = 9.5$ Hz, =C(N)), 148.0 (d, $J = 16.2$ Hz, $\beta$-C(COOMe)), 145.9 (d, $J = 37.2$ Hz, $\alpha$-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)), 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 (OCH$_3$), 52.3 (OCH$_3$), 51.2 (2×CH–N), 23.6 (2×CH$_3$), 22.2 (2×CH$_3$). Exact mass: calcd for C$_{31}$H$_{30}$NO$_9$PW, 774.1161; found, 774.1141. Anal. Calcd. for C$_{31}$H$_{30}$NO$_9$PW: C, 48.02; H, 3.90; N, 1.81. Found: C, 47.62; H, 3.78; N, 1.89.

3.6 References


1988, 348, 361.


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.


Panichakul, D.; Mathey, F. Presented at the PERCH-CIC Congress VII, 4-7 May 2011, Chonburi, Thailand.
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 \(2\pi\) 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 \(2\pi\) aromaticity,\(^3\) this cation appears to be quite difficult to make and must be kept in liquid SO\(_2\) at low temperature. Since then, there has been no report on this type of chemistry.

![Scheme 4.1](image1)

![Scheme 4.2](image2)

The reasons for our renewed intent in these species lied in the puzzling instability of this \(2\pi\)-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, 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 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-phenylaminophosphirane 166.

![Scheme 4.3](attachment:image.png)
The reaction of \([\text{PhNHP–W(CO)}_5]\) as generated from 166 as mentioned above with \(\text{PhCCN}^\text{iPr}_2\) was performed in boiling toluene. It led us to the expected 1,2-diaminophosphirene (168) in good yield (Scheme 4.4).

As expected, phosphirene 168 shows high-field shift of the \(^{31}\text{P}\) resonance at \(-97.8\) ppm (\(^1J_{PW} = 306.8\) Hz, \(^2J_{PNH} = 26.3\) 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.
The structure of the 2-aminophosphindole (170) was established by X-ray crystal structure analysis (Figure 4.2). The selected bond lengths (Å) and angles (°) 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. 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.

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Bond angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(1)−O(6)</td>
<td>1.559(9)</td>
</tr>
<tr>
<td>P(1)−C(6)</td>
<td>1.815(2)</td>
</tr>
<tr>
<td>P(1)−C(13)</td>
<td>1.895(2)</td>
</tr>
<tr>
<td>C(13)−N(1)</td>
<td>1.292(3)</td>
</tr>
<tr>
<td>C(13)−C(12)</td>
<td>1.502(3)</td>
</tr>
<tr>
<td>C(12)−C(11)</td>
<td>1.507(3)</td>
</tr>
<tr>
<td>C(6)−C(11)</td>
<td>1.398(3)</td>
</tr>
</tbody>
</table>
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-$\beta$-chboroethylphosphirenes.$^{29}$ Preliminary experiments were carried out with the phosphanorbornadiene complex 163 and PhCCN$^\text{Pr}_2$ in boiling toluene. They generated not only 1-$\beta$-chboroethylphosphirene 171 but also 1,2-diphosphetene 172 in moderate yields.

\[
\begin{array}{c}
\text{163} \quad \text{toluene, 110 °C} \quad \text{171 (21%) \quad 172 (21%)}
\end{array}
\]

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 $\beta$-chboroethyl 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$_2$Cl 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 (R = Ph, Me)$^5$ to demonstrate the generality of this ring expansion. Phosphindoles 173-175 were obtained in moderated yields (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 BH$_3$ (Figure 4.4), chosen as the simplest representative Lewis acid. We suspected that BH$_3$ 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.

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Bond angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(1)–C(6)</td>
<td>1.8032(1)</td>
</tr>
<tr>
<td>P(1)–C(13)</td>
<td>1.8503(1)</td>
</tr>
<tr>
<td>C(12)–C(13)</td>
<td>1.3672(2)</td>
</tr>
<tr>
<td>C(11)–C(12)</td>
<td>1.4459(2)</td>
</tr>
<tr>
<td>C(6)–C(11)</td>
<td>1.4019(2)</td>
</tr>
<tr>
<td>C(13)–N(1)</td>
<td>1.3640(2)</td>
</tr>
</tbody>
</table>
Figure 4.4 A structure between the aminophosphirene complex 176 and BH₃.

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.

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Bond angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(16)–C(1)</td>
<td>C(1)–P(16)–C(2) 44.48</td>
</tr>
<tr>
<td>P(16)–C(2)</td>
<td>P(16)–C(1)–C(28) 123.61</td>
</tr>
<tr>
<td>C(1)–C(2)</td>
<td>P(16)–C(1)–B(41) 111.77</td>
</tr>
<tr>
<td>C(1)–B(41)</td>
<td>1.755</td>
</tr>
<tr>
<td>C(2)–N(7)</td>
<td>1.306</td>
</tr>
</tbody>
</table>
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)\textsuperscript{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 \textsuperscript{6}HexCCN\textsuperscript{7}Pr\textsubscript{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 (179\textsubscript{a,b}) 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, $^{1}J_{HP} = 346.0$ Hz, $^{1}J_{PW} = 298.1$ Hz, major; δ $^{31}$P(179b) +59.9, $^{1}J_{HP} = 337.0$ Hz, $^{1}J_{PW} = 302.0$ 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.

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Bond angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(1)–C(13)</td>
<td>1.867(1)</td>
</tr>
<tr>
<td>P(1)–O(1)</td>
<td>1.63(2)</td>
</tr>
<tr>
<td>O(1)–B(1)</td>
<td>1.520(1)</td>
</tr>
<tr>
<td>C(13)–N(1)</td>
<td>1.471(1)</td>
</tr>
<tr>
<td>N(1)–C(25)</td>
<td>1.327(1)</td>
</tr>
<tr>
<td>N(1)–C(22)</td>
<td>1.520(1)</td>
</tr>
<tr>
<td>C(13)–C(14)</td>
<td>1.322(1)</td>
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<td></td>
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</tbody>
</table>
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-d4. 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 seperations. All commercially available reagents were used as received from the suppliers.
4.5.1 Synthesis of β-chloroethynyl(phenylamino)phosphe 164\(^{10}\)

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{Cl} \\
\text{PhHN} - \overset{\text{P}}{\text{W}}(\text{CO})_5 \\
\text{H}
\end{align*}
\]

164

7-β-Chloroethyl 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). \(^{31}\)P NMR (162 MHz, CDCl\(_3\)): \(\delta +1.5\) (s, \(^1J_{PW} = 254.0\) Hz, \(^1J_{PH} = 366.0\) Hz). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.40-6.80\) (m, 5H, Ar\(H\)), 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, \(CH_2P\)), 2.63 (m, 2H, \(CH_2Cl\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 197.5\) (d, \(J = 23.8\) Hz, \(\text{trans} \ \text{CO}\)), 195.4 (d, \(J = 23.8\) Hz, \(\text{cis} \ \text{CO}\)), 39.5 (s, \(CH_2Cl\)), 32.9 (d, \(J = 25.3\) Hz, P\(CH_2\)).

4.5.2 Synthesis of 1-phenaminophosphirane 166\(^{10}\)

\[
\begin{align*}
\text{(OC)}_3\text{W} \\
\overset{\text{P}}{\text{NPh}}
\end{align*}
\]

166

Phosphane complex 164 (0.614 g, 1.20 mmol), in 15 mL of THF was cooled to \(-40^\circ\)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). \(^{31}\)P NMR (162 MHz, CDCl\(_3\)): \(\delta -132.0\) (s, \(^1J_{PW} = 288\) Hz). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.24-6.88\) (m, 5H, Ar\(H\)), 3.97 (br s, 1H, N\(H\)), 1.63-1.17 (m, 4H, 2×\(CH_2\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 198.0\) (d, \(J = 34.6\) Hz, \(\text{trans} \ \text{CO}\)), 195.3 (d, \(J = 8.5\) Hz, \(\text{cis} \ \text{CO}\)), 14.0 (d, \(J = 13.1\) Hz, \(CH_2CH_2\)).
4.5.3  Preparation of phosphirene 168

![Chemical structure](image)

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$_3$): $\delta$ –97.8 (s, $^1J_{PW}$ = 306.8 Hz, $^2J_{PNH}$ = 26.3 Hz). $^1$H NMR (400 MHz, CDCl$_3$, –50 °C): $\delta$ 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): $\delta$ 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 C$_{25}$H$_{25}$N$_2$O$_5$PW: 648.1010; Found: 648.1016.

4.5.4  Preparation of phosphirene 177

![Chemical structure](image)
The 1-aminophosphirane complex 166 (0.237 g, 0.50 mmol) and $N,N$-diisopropylct-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%). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ –101.0 (s, $^1J_{PW} = 308.3$ Hz). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.17 (t, $J = 8.2$ Hz, 2H, ArH), 6.94 (t, $J = 7.4$ Hz, 1H, ArH), 6.74 (d, $J = 7.7$ Hz, 2H, ArH), 4.00 (d, $^2J_{PH} = 22.7$ Hz, 1H, NH), 3.74 (br s, 2H, 2×CH), 2.49-2.42 (m, 2H, CH$_2$), 1.67-1.59 (m, 2H, CH$_2$), 1.42-1.30 (m, 6H, 3×CH$_2$), 1.29-1.19 (m, 12H, 4×CH$_3$), 0.90 (t, $J = 6.8$ Hz, 3H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 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 (CH$_2$), 29.2 (CH$_2$), 28.3 (d, $J = 3.6$ Hz, CH$_2$), 26.8 (d, $J = 3.1$ Hz, CH$_2$), 22.5 (CH$_2$), 21.8 (4×CH$_3$), 14.0 (CH$_3$). Exact mass: calcd. for C$_{25}$H$_{33}$N$_2$O$_5$PW: 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
31P NMR (122 MHz, CD2Cl2): δ +143.6 (s, 1J_PW= 266.0 Hz). 1H NMR (400 MHz, CD2Cl2): 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×CH), 3.45-3.36 (m, 2H, CH2Cl), 2.42-2.34 (m, 2H, CH2), 1.44 (d, J = 6.8 Hz, 6H, 2×CH3), 1.39 (d, J = 8.4 Hz, 2×CH3). 13C NMR (100 MHz, CDCl3): 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, =C(N)), 130.6 (s, ipso ArC), 128.8 (s, meta ArCH), 127.9 (d, J = 6.6 Hz, ortho ArCH), 126.4 (s, para ArCH), 114.1 (s, =CP), 52.1 (CH), 52.0 (CH), 42.5 (d, J = 14.3 Hz, CH2), 40.3 (CH2), 22.5 (2×CH3), 22.0 (2×CH3). Exact mass: calcd for C21H23ClNO5PW 619.0512, found: 619.0523.

4.5.5.2 Diphosphetene 172

\[ \text{Ph} \quad \text{N} \quad \text{Pr}_2 \quad \text{(OC)}_5 \text{W-P-P-...CH}_2 \text{CH}_2 \text{Cl} \quad \text{ClH}_2 \text{CH}_2 \text{C} \quad \text{W(CO)}_5 \]

172

31P NMR (162 MHz, CD2Cl2): δ +39.1 (d, 1J_PW = 229.4 Hz, 1J_PP = 24.3 Hz), 2.90 (d, 1J_PW = 243.6 Hz, 1J_PP = 23.7 Hz). 1H NMR (400 MHz, CD2Cl2): 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×CH, CH2Cl), 3.86-3.82 (m, 2H, CH2Cl), 3.26-3.10 (m, 2H, CH2), 3.09-2.98 (m, 2H, CH2), 1.37 (d, J = 7.1 Hz, 6H, 2×CH3), 1.32 (d, J = 6.7 Hz, 6H, 2×CH3). 13C NMR (100 MHz, CD2Cl2): 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×ArCH), 128.5 (ArCH), 128.4 (ArCH), 128.3 (ArCH), 114.8 (dd, J = 20.0 and 39.0 Hz, =CP), 53.7 (CH), 53.6 (CH), 43.8 (2×CH2), 41.0 (2×CH2), 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

![Image of phosphindole complex 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**

![Phosphindole 173](image)

Yield: 25.0 mg (40%). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ +5.2 (s, $^1J_{PW} = 228.2$ Hz, $^2J_{PH} = 22.5$ Hz). $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ 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×CH), 3.40-3.32 (m, 1H, CHCl), 3.09-3.01 (m, 1H, CH), 2.73-2.70 (m, 2H, CH$_2$), 1.40 (d, $J = 6.7$ Hz, 6H, 2×CH$_3$), 1.38 (d, $J = 6.8$ Hz, 6H, 2×CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 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×CH$_3$), 20.0 (2×CH$_3$). Exact mass: calcd for C$_{21}$H$_{23}$ClNO$_5$PW 619.0512, found: 619.0518.

**4.5.7.2 Phosphindole 174**

![Phosphindole 174](image)

Yield: 39.0 mg (62%). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ +14.7 (s, $^1J_{PW} = 229.3$ Hz). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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×CH$_2$), 1.33 (d, $J = 6.7$ Hz, 12H, 4×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×CH$_3$), 19.8 (2×CH$_3$).

Exact mass: calcd for C$_{25}$H$_{24}$NO$_5$PW 633.0901, found: 633.0904.

4.5.7.3 Phosphindole 175

Yield: 33 mg (56%). $^{31}$P NMR (162 MHz, CDCl$_3$): δ +118.9 (s, $^{1}J_{PW} = 280.3$ Hz). $^1$H 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×CH$_2$), 3.37 (d, $J = 12.1$ Hz, 3H, OCH$_3$), 1.39 (d, $J = 6.8$ Hz, 6H, 2×CH$_3$), 1.35 (d, $J = 6.8$ Hz, 6H, 2×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 C$_{20}$H$_{22}$NO$_6$PW 587.0694, found: C, 587.0696.
4.5.8 Aniline-borane adduct 178 and secondary phosphine complexes 179ab.

Phosphirene 177 (0.145 g, 0.22 mmol) 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

\[ \text{PhNH}_2\text{B(C}_6\text{F}_5)_3 \]

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, ²J = 238.0 Hz, ortho ArCF), 140.3 (d, ²J = 250.0 Hz, para ArCF), 137.2 (d, ²J = 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, ³J = 20.0 Hz, 6F, ortho ArCF), −155.6 (t, ³J = 21.4 Hz, 3F, para ArCF), −162.4 (td, ³J = 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

\[ \text{P}^\text{N}^\text{Me}_{3} \text{Me}^\text{Pr}^\text{Hex} \text{OB(C}_6\text{F}_5)_3^\text{W(CO)}_5 \]

Yield: 60.2 mg (25%). ³¹P NMR (162 MHz, CDCl₃): δ +68.8 (s, ¹J = 298.0 Hz, ¹J = 346.2 Hz, major isomer), +59.9 (s, ¹J = 302.4 Hz, ¹J = 337.4 Hz, minor isomer). Selected ¹³C NMR data (400 MHz, CDCl₃, major isomer): δ 195.8 (d, ²J = 8.0 Hz, ³J = 41.8 Hz, major isomer).
Hz, \textit{cis} CO), 192.0 (s, C=N+), 147.8 (d, \(J = 28.0\) Hz, =CH); \(^{19}\text{F}\) NMR (376 MHz, CDCl\(_3\)): \(\delta -132.3\) (d, \(^3\text{J}_{\text{FF}} = 23.1\) Hz, 6F, minor isomer of \textit{ortho} ArCF), \(-132.6\) (d, \(^3\text{J}_{\text{FF}} = 24.7\) Hz, 6F, major isomer of \textit{ortho} ArCF), \(-158.6\) (t, \(^3\text{J}_{\text{FF}} = 22.3\) Hz, 3F, minor isomer of \textit{para} ArCF), \(-158.9\) (t, \(^3\text{J}_{\text{FF}} = 21.6\) Hz, 3F, major isomer of \textit{para} ArCF), \(-164.4\) (m, 6F, \textit{meta} ArCF).

\textbf{4.6 References}


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-1H-phosphirene

Reported in 1995 by Deschamps and Mathey, 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(δ⁺)–Cl(δ⁻) 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.

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 W(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.

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<th>Conditions</th>
<th>Results</th>
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<td>UV, 3 h</td>
<td>decomposition of 183</td>
</tr>
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</table>

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 PhPCl₂ and AlCl₃ with diphenylacetylene was carried out in CH₂Cl₂ 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 Bu₃P at 0 °C for 15 h to afford the expected 1,2,3-triphenylphosphirene 3 in moderate yield.⁴

![Scheme 5.3](image-url)
Another approach leading to the 1,2,3-triphenylphosphirene 3 using the decomplexation technique\(^5\) 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.

\[
\begin{array}{c}
\text{Ph} \quad \text{Ph} \quad \text{P} \quad \text{W(CO)} \quad \text{I}_2, \text{CH}_2\text{Cl}_2 \\
\text{Ph} \quad \text{Ph} \quad 25 \degree \text{C}, 30 \text{ min} \\
\text{Ph} \quad \text{Ph} \quad \text{P} \quad \text{W(CO)} \quad \\text{I}_2 \quad \text{Ph} \\
\text{Ph} \quad \text{N-Methylimidazole} \\
\text{Ph} \quad \text{Ph} \quad \text{N-Methylimidazole} \\
\end{array}
\]

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 \(^1\)H 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 literature\textsuperscript{7} 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 $\text{194a}$ and $\text{194b}$ (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).
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 °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.

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.
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 S₈, we could get the phosphirene sulfide. To our surprise, we were unable to get the expected product. We observed various peaks on ³¹P 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 S₈ in boiling toluene. The progress of this reaction was monitored by ³¹P 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.
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). 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 5.10

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. 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](image)

**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.\(^\text{11,12}\) 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 [PhP=S] with 2,3-dimethyl-1,3-butadiene gives 201 in 38% yield.

![Scheme 5.13](image)

**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 $\delta$ values and is frequency referenced relative to tetramethylsilane for $^1$H 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-$\beta$-chloroethylphosphirene (180) (0.697 g, 1.17 mmol) in reaction flask, dry CH$_2$Cl$_2$ 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$_4$Cl was added to quench the reaction. Extraction by using CH$_2$Cl$_2$ and wash the organic layer with H$_2$O 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$_3$): $\delta$ –109.6 (s, $^1J_{PW} = 327.0$ Hz).

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

![Structure of 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$_3$): $\delta$ –60.7 (s).

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

![Structure of 2,3-Diphenyl-1-vinyl-1H-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$_3$): $\delta$ –185.8 ($^2J_{PH} = 32.3$ Hz, $^3J_{PH} = 15.0, 5.0$ Hz). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 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, C).
Hz, CH₃), 123.7 (d, J = 42.0 Hz, C). Exact mass: calcd for C₁₀H₁₃P 236.0755, found: 236.0761.

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

\[
\begin{array}{c}
\text{Ph} \\
\text{F} \\
\text{Ph}
\end{array}
\]

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)

\[
\begin{array}{c}
\text{Ph} \\
\text{P} \\
\text{Ph}
\end{array}
\]

\[
\begin{array}{c}
\text{Ph} \\
\text{S} \\
\text{Ph}
\end{array}
\]

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$_2$Cl$_2$ 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$_3$): $\delta$ –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$_3$): $\delta$ +65.2 (s). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.89-7.83 (m, 2H, ArH), 7.46-7.34 (m, 3H, ArH), 3.59 (t, $J = 15.1$ Hz, 1H, CH), 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 C$_{12}$H$_{18}$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\(_3\)): \(\delta +98.7\) (s, major isomer) and +86.3 (s, minor isomer). \(^1\)H NMR (400 MHz, CDCl\(_3\)) of major isomer and minor isomer: \(\delta 7.82\) (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\(_3\)):

- 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 C\(_{21}\)H\(_{19}\)OPS 350.0894 found: 350.0899.

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

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{Ph} & \quad \text{P} \quad \text{Mo(CO)}_5
\end{align*}
\]

195

To a stirred suspension of molybdenum carbonyl (7.70 g, 29.3 mmol) in 20 mL CH\(_2\)CN, was added Me\(_3\)NO.2H\(_2\)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 Mo(CO)\(_5\)(CH\(_3\)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$_3$): $\delta$ +31.7 (s). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.51-7.45 (m, 2H, ArH), 7.37-7.34 (m, 3H, ArH), 6.52 (d, $J = 37.6$ Hz, 2H, 2×CH), 2.12 (s, 6H, 2×CH$_3$).

5.4.9 Preparation of 1-phenylphosphanorbornadiene molybdenum complex (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$_3$): $\delta$ +239.0 (s).

5.4.10 Synthesis of phosphirene 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, CDCl₃): 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

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). ³¹P NMR (162 MHz, CDCl₃): δ +38.7 (s). ¹H NMR (400 MHz, CDCl₃): 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, CH₂), 2.83 (d, J = 16.0 Hz, CHH), 1.69 (s, 3H, CH₃), 1.54 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃): 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, CH₃), 32.5 (d, J = 2.5 Hz, CH₃), 21.5 (d, J = 4.8 Hz, CH₃). Exact mass: calcd for C₁₇H₁₅O₅PSMo 459.9432, found: 459.9433.

5.4.12 Synthesis of 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$_3$): $\delta$ +32.4 (s). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 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 (2xCH), 130.4 (2xCH), 129.6 (CH), 129.5 (CH), 129.0 (CH), 128.7 (2xCH), 128.3 (CH), 128.2 (2xCH), 128.1 (CH), 127.7 (CH), 51.4 (OCH$_3$). Exact mass: calcd for C$_{21}$H$_{19}$O$_2$P 334.1123, found: 334.1121.

5.4.13 Synthesis of 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$_2$Cl$_2$ (80:20) to give 201 (7.0 mg, 38% yield). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ +45.7 (s). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.90-7.85 (m, 2H, ArH), 7.54-7.45 (m, 3H, ArH), 3.07 (d, $J = 9.6$ Hz, 4H, 2xCH$_2$), 1.80 (s, 3H, 2xCH$_3$). Exact mass: calcd for C$_{12}$H$_{15}$PS 222.0632, found: 222.0636.
5.5 References


APPENDIX

**Table A1** Crystallographic Data for compound 134

![Diagram of compound 134]

- **Empirical formula**: C22 H19 O5 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
  - $b = 9.7533(3)$ Å
  - $c = 12.4712(4)$ Å
  - $\alpha = 90^\circ$
  - $\beta = 90.589(2)^\circ$
  - $\gamma = 90^\circ$
- **Volume**: 1165.00(6) Å³
- **Z**: 2
- **Density (calculated)**: 1.728 Mg/m³
- **Absorption coefficient**: 5.107 mm⁻¹
- **F(000)**: 588
- **Crystal size**: 0.30 x 0.20 x 0.06 mm³
- **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 F²
- **Data / restraints / parameters**: 10244 / 429 / 548
- **Goodness-of-fit on F²**: 1.065
- **Final R indices [I>2sigma(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

![Chemical Structure](image)

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</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0323, wR2 = 0.0712</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0581, wR2 = 0.0916</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>1.727 and -2.154 eÅ$^{-3}$</td>
</tr>
</tbody>
</table>
**Table A3** Crystallographic Data for compound 155

![Chemical Structure](image)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C26 H25 N O10 P2 W2</td>
</tr>
<tr>
<td>Formula weight</td>
<td>941.11</td>
</tr>
<tr>
<td>Temperature</td>
<td>173(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2(1)/n</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>a = 13.2742(4) Å</td>
<td>α = 90°</td>
</tr>
<tr>
<td>b = 12.2704(4) Å</td>
<td>β = 108.164(2)°</td>
</tr>
<tr>
<td>c = 20.1250(6) Å</td>
<td>γ = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>3114.61(17) Å</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>2.007 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>7.536 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>1784</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.40 x 0.20 x 0.20 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.63 to 37.00°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-19&lt;=h&lt;=22, -20&lt;=k&lt;=20, -34&lt;=l&lt;=23</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>92462</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>15624 [R(int) = 0.0319]</td>
</tr>
<tr>
<td>Completeness to theta = 37.00°</td>
<td>98.5 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.3141 and 0.1525</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>15624 / 115 / 436</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.190</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0262, wR2 = 0.0677</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0442, wR2 = 0.0888</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>1.416 and -1.504 e.Å⁻³</td>
</tr>
</tbody>
</table>
**Table A4 Crystallographic Data for compound 158**

![Image of compound 158]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C34 H44 N2 O4</td>
</tr>
<tr>
<td>Formula weight</td>
<td>544.71</td>
</tr>
<tr>
<td>Temperature</td>
<td>173(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>Cc</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>22.0421(6) Å</td>
</tr>
<tr>
<td>b</td>
<td>11.3051(3) Å</td>
</tr>
<tr>
<td>c</td>
<td>15.4125(7) Å</td>
</tr>
<tr>
<td>Volume</td>
<td>3093.15(18) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.170 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.076 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>1176</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.14 x 0.12 x 0.10 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.14 to 25.24°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-22&lt;=h&lt;=26, -13&lt;=k&lt;=13, -18&lt;=l&lt;=18</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>12283</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>4910 [R(int) = 0.0366]</td>
</tr>
<tr>
<td>Completeness to theta = 25.24°</td>
<td>98.1 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9924 and 0.9894</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>4910 / 2 / 371</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.129</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0434, wR2 = 0.1129</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0587, wR2 = 0.1385</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.427 and -0.281 e.Å⁻³</td>
</tr>
</tbody>
</table>
### Table A5 Crystallographic Data for compound 170

![Structure of compound 170](image)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C37.50 H20.50 B Cl1.50 F15 N O6 P W</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1144.85</td>
</tr>
<tr>
<td>Temperature</td>
<td>103(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>$a = 11.2518(5)$ Å</td>
<td>$\alpha = 77.600(2)^\circ$</td>
</tr>
<tr>
<td>$b = 11.4277(5)$ Å</td>
<td>$\beta = 78.274(2)^\circ$</td>
</tr>
<tr>
<td>$\alpha = 16.4537(8)$ Å</td>
<td>$\gamma = 72.811(2)^\circ$</td>
</tr>
<tr>
<td>Volume</td>
<td>1951.73(15) Å</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.948 Mg/m$^3$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>3.224 mm$^{-1}$</td>
</tr>
<tr>
<td>$F(000)$</td>
<td>1110</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.28 x 0.10 x 0.04 mm$^3$</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.89 to 37.69$^\circ$</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-19$\leq h \leq 17$, -19$\leq k \leq 19$, -28$\leq l \leq 28$</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>55516</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>20390 [R(int) = 0.0412]</td>
</tr>
<tr>
<td>Completeness to theta = 37.69$^\circ$</td>
<td>97.9 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.8819 and 0.4655</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on $F^2$</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>20390 / 30 / 599</td>
</tr>
<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>1.063</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0357, wR2 = 0.0799</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0488, wR2 = 0.0935</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>1.912 and -1.736 e.Å$^{-1}$</td>
</tr>
</tbody>
</table>
### Table A6 Crystallographic Data for compound 174

![Chemical Structure](image.png)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C25 H24 N O5 P W</td>
</tr>
<tr>
<td>Formula weight</td>
<td>633.27</td>
</tr>
<tr>
<td>Temperature</td>
<td>103(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2(1)/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>(a) = 16.1263(3) Å</td>
<td>(\alpha = 90^\circ).</td>
</tr>
<tr>
<td>(b) = 9.4786(2) Å</td>
<td>(\beta = 127.4470(10)^\circ).</td>
</tr>
<tr>
<td>(c) = 20.0072(3) Å</td>
<td>(\gamma = 90^\circ).</td>
</tr>
<tr>
<td>Volume</td>
<td>2427.95(8) Å³</td>
</tr>
<tr>
<td>(Z)</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.732 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>4.859 mm⁻¹</td>
</tr>
<tr>
<td>(F(000))</td>
<td>1240</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.40 x 0.36 x 0.30 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>3.35 to 43.48°.</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-30&lt;=h&lt;=31, -18&lt;=k&lt;=17, -38&lt;=l&lt;=38</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>64898</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>18315 [R(int) = 0.0376]</td>
</tr>
<tr>
<td>Completeness to theta = 43.48°</td>
<td>99.1 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.3235 and 0.2467</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on (F^2)</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>18315 / 0 / 302</td>
</tr>
<tr>
<td>Goodness-of-fit on (F^2)</td>
<td>1.006</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0252, wR2 = 0.0503</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0440, wR2 = 0.0556</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>2.642 and -1.576 e.Å⁻³</td>
</tr>
</tbody>
</table>
**Table A7** Crystallographic Data for compound 179ab

![Chemical Structure](image)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C37 H28 B F15 N O6 P W</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1093.23</td>
</tr>
<tr>
<td>Temperature</td>
<td>103(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>(a)</td>
<td>10.8060(4) Å</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>69.386(2)°</td>
</tr>
<tr>
<td>(b)</td>
<td>13.2637(5) Å</td>
</tr>
<tr>
<td>(\beta)</td>
<td>87.030(2)°</td>
</tr>
<tr>
<td>(c)</td>
<td>15.0392(5) Å</td>
</tr>
<tr>
<td>(\gamma)</td>
<td>82.802(2)°</td>
</tr>
<tr>
<td>Volume</td>
<td>2001.55(12) Å³</td>
</tr>
<tr>
<td>(Z)</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.814 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>3.042 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>1068</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.40 x 0.30 x 0.10 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.45 to 30.50°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-15&lt;=h&lt;=15, -18&lt;=k&lt;=18, -21&lt;=l&lt;=21</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>49578</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>12095 [R(int) = 0.0433]</td>
</tr>
<tr>
<td>Completeness to theta = 30.50°</td>
<td>99.1 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.7507 and 0.3758</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>12095 / 1027 / 1014</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.068</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0459, wR2 = 0.1123</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0689, wR2 = 0.1311</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>2.521 and -2.529 e.Å⁻³</td>
</tr>
</tbody>
</table>