Advances in organophosphorus chemistry
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Chapter 1

N-heterocyclic Carbene-Phosphinidene Adducts: Synthesis, Properties and Applications

Abstract: Syntheses, properties, and reactivity of N-heterocyclic carbene-phosphinidene adducts are reviewed. These adducts, formally built by combining a phosphinidene with a carbene, are characterized by high nucleophilicity at the phosphorus atom. The main types of reactivity these adducts exhibit are: Lewis-base reactivity towards main group and organic compounds as well as transition-metal complexes, substitution reactions at the phosphorus atom with main group compounds and transition-metal complexes, and phosphinidene transfer reactions resulting in C–P bond cleavage. These differ substantially from the classic phosphaalkenes.

1.1 Introduction

The combination of a low-valent N-heterocyclic carbene\textsuperscript{[1]} and a transient phosphinidene\textsuperscript{[2]} creates an electron-rich phosphaalkene that was highlighted for the first time by Arduengo and co-workers in 1997\textsuperscript{[3]} and early examples were reported by Schmidpeter in 1980 (Scheme 1).\textsuperscript{[4]} These N-heterocyclic carbene-phosphinidene adducts are an emerging class of compounds that have seen tremendous advances in the past five years and developed from laboratory curiosities to important main-group species that can undergo a plethora of transformations. Hence, this review provides a complete overview of the chemistry of these species to date, where we focus on phosphinidenes stabilized by N-heterocyclic carbenes (NHCs),\textsuperscript{[5]} particularly bis(amino)carbenes and (alkyl)(amino)carbenes (CAACs).\textsuperscript{[6]}

![Scheme 1. The first reported examples by Schmidpeter and Arduengo et al. (top) and canonical forms of NHC-phosphinidene adducts, X = CR\textsubscript{2}, NR or S (bottom).](image)

Carbene-phosphinidene adducts (NHC=PR) can be regarded as inversely polarized phosphaalkenes\textsuperscript{[7]} and are represented by the three canonical forms A-C (Scheme 1). Resonance form A features a formal P=C double bond, B a zwitterion with a P–C single bond, and C displays a dative C→P donor–acceptor interaction, which indicates that carbene-phosphinidene adducts are nucleophilic P-donor ligands with two potentially available lone pairs of electrons. The exact description
of a given NHC=PR adduct depends on the phosphorus substituent and the nature of the carbene.

In this chapter, we highlight all synthetic approaches leading to N-heterocyclic carbene-phosphinidene adducts, focus on the nature of the chemical bond between the carbene and phosphinidene moieties and provide an overview of the reactivity of the NHC=PR adducts towards main group compounds, transition-metal complexes and organic electrophiles. All the carbene-phosphinidene adducts discussed in this chapter are summarized in Table 1, and ordered according to the stabilizing carbene and size of the P substituent, starting with phosphinidene adducts of imidazolylidenes (1-9), followed by those of imidazolinylidenes (10, 11), amido carbenes (12-14), tetrahydropyrimidinylidenes (15, 16), thiazolylidene (17) and finally cyclic (alkyl)(amino)carbenes (CAACs: 18-22). For simplicity, we display all carbene-phosphinidene adducts in this chapter in resonance form A.

Table 1. $^{31}$P, $^{13}$C NMR chemical shifts ($P=C_{NHC}$) (recorded in C$_6$D$_6$ unless stated otherwise) and selected structural data for the adducts 1-PR–22-PR.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Name$^{[a]}$</th>
<th>$\delta^{31}$P, ppm</th>
<th>$\delta^{13}$C, ppm</th>
<th>C$_{NHC}=P$ bond, Å</th>
<th>C-P-R angle, °</th>
<th>Torsion angle N-C-P-R, °</th>
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<tr>
<td>1·PH$^{[8]}$</td>
<td>149.3</td>
<td>176.0</td>
<td>1.763(3)</td>
<td>96.0(15)</td>
<td>0.9(18)</td>
<td></td>
</tr>
<tr>
<td>1·PPh$^{[9]}$</td>
<td>-49.1</td>
<td>170.1</td>
<td>1.7917(14)</td>
<td>101.30(6)</td>
<td>48.01(16)</td>
<td>[1.7911(15)] $^{[a]}$</td>
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<tr>
<td>1·PMes$^{[10]}$</td>
<td>-73.8</td>
<td>169.9</td>
<td>1.768(4)</td>
<td>104.6(2)</td>
<td>32.5(4)</td>
<td></td>
</tr>
<tr>
<td>2·PH$^{[8]}$</td>
<td>-148.8</td>
<td>174.7$^{[b]}$</td>
<td>1.7721(14)</td>
<td>95.9(8)</td>
<td>0.2(8)</td>
<td></td>
</tr>
<tr>
<td>(2-H)$^{[11]}$ PCHN(iPr)$_2$</td>
<td>-64.8$^{[c]}$</td>
<td>178.9$^{[d]}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Chapter 1

\[
\begin{align*}
\text{2-PPh}^3 & : -53.5^b, 169.1^b, 1.794(3), 102.34(14), 51.0(3) \\
\text{2-PMes}^{12} & : -75.1, - , - , - , - \\
\text{2-P(Dmp)}^{13} & : -76.7, - , 1.786(4), 99.10(17), 55.5(4) \\
\text{2-P(EMind)}^{14} & : -70.5, 168.3, - , - , - \\
\text{2-P(Eind)}^{14} & : -63.9, 168.6, 1.767(3), 102.72(12), 3.4(3) \\
\text{3-PH}^8 & : -149.9^b, 173.7^b, - , - , - \\
\text{3-PPh}^{15,16} & : -61.2^{15}, 167.8^{15}, - , - , - \\
\text{3-P(pTol)}^{16} & : -57.0^c, - , - , - , - \\
\text{3-P(DAP)}^{17} & : -68.2 \text{ P}^1 \text{ (177.3 P}^3) \text{), 166.8, - , - , - } \\
\text{4-P(Dmp)}^{13} & : -75.0, 171.3, 1.799(3), 101.53(11), 57.1(2)
\end{align*}
\]
### N-heterocyclic Carbene-Phosphiniden Adducts: Synthesis, Properties and Applications

<table>
<thead>
<tr>
<th>Adduct</th>
<th>Bond Angle (°)</th>
<th>Bond Length (Å)</th>
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<tbody>
<tr>
<td><strong>5·PH</strong>&lt;sup&gt;[18]&lt;/sup&gt;</td>
<td>-147&lt;sup&gt;[18]&lt;/sup&gt;</td>
<td>1.747(3) 100(2) 5(2)</td>
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<td></td>
<td>-147.3&lt;sup&gt;[19]&lt;/sup&gt;</td>
<td>180.0&lt;sup&gt;[19]&lt;/sup&gt; 1.747(2) 101(2) 3(2)</td>
</tr>
<tr>
<td><strong>5·PCF&lt;sub&gt;3&lt;/sub&gt;</strong>&lt;sup&gt;[19]&lt;/sup&gt;</td>
<td>-23.6</td>
<td>168.1 1.784(2) 101.66(8) 31.3(2)</td>
</tr>
<tr>
<td><strong>5·PPh</strong>&lt;sup&gt;[19]&lt;/sup&gt;</td>
<td>-23.0</td>
<td>170.0&lt;sup&gt;[20]&lt;/sup&gt; 1.763(6) 99.9(3) 26.5(7)</td>
</tr>
<tr>
<td><strong>5·PMes</strong>&lt;sup&gt;[12]&lt;/sup&gt;</td>
<td>-59.1</td>
<td>- 1.769(3) 104.90(11) 8.3(3)</td>
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<tr>
<td><strong>5·PGePh&lt;sub&gt;3&lt;/sub&gt;</strong>&lt;sup&gt;[20]&lt;/sup&gt;</td>
<td>-155.2&lt;sup&gt;[20]&lt;/sup&gt;</td>
<td>168.7&lt;sup&gt;[20]&lt;/sup&gt; - - -</td>
</tr>
<tr>
<td><strong>5·PSnPh&lt;sub&gt;3&lt;/sub&gt;</strong>&lt;sup&gt;[20]&lt;/sup&gt;</td>
<td>-179.5&lt;sup&gt;[20]&lt;/sup&gt;</td>
<td>169.4&lt;sup&gt;[20]&lt;/sup&gt; 1.778(3) 111.51(9) 7.1(3)</td>
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<tr>
<td><strong>6·PH</strong>&lt;sup&gt;[21,22,23]&lt;/sup&gt;</td>
<td>-134.3&lt;sup&gt;[21]&lt;/sup&gt;</td>
<td>180.5&lt;sup&gt;[21]&lt;/sup&gt; - - -</td>
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<tr>
<td></td>
<td>-136.7&lt;sup&gt;[22]&lt;/sup&gt;</td>
<td>180.2&lt;sup&gt;[22]&lt;/sup&gt; 1.752(1)&lt;sup&gt;[22]&lt;/sup&gt; 94.5(7) 1.2(6)</td>
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<td>-133.8&lt;sup&gt;[23]&lt;/sup&gt;</td>
<td>180.9&lt;sup&gt;[23]&lt;/sup&gt; 1.7509(15)&lt;sup&gt;[23]&lt;/sup&gt; 94.9(12) 1.4(10)</td>
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<td><strong>6·PPh</strong>&lt;sup&gt;[15,24]&lt;/sup&gt;</td>
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<td>172.9&lt;sup&gt;[15]&lt;/sup&gt; - - -</td>
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<td>-19.4&lt;sup&gt;[24]&lt;/sup&gt;</td>
<td>- 1.7658(10)&lt;sup&gt;[24]&lt;/sup&gt; 104.61(4) 24.5</td>
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<td>19-PSiCl$_3$$^{[32]}$</td>
<td>-22.0$^{[b]}$</td>
<td>217.4$^{[b]}$</td>
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### N-heterocyclic Carbene-Phosphinidene Adducts: Synthesis, Properties and Applications

<table>
<thead>
<tr>
<th>Adduct</th>
<th>Structure</th>
<th>Bond Angle (°)</th>
<th>Dihedral Angle (°)</th>
<th>Bond Length (Å)</th>
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<td>-</td>
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<td>214.3</td>
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<td>-</td>
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<td>(96.3 %)</td>
<td>208.2</td>
<td>1.74(12)</td>
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<td>(Z\cdot PCl)</td>
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<td>98.3(7)</td>
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<td>(20\cdot P(DAP))</td>
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<td>76.3 P¹ (156.6 P²)</td>
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<td>(E\cdot PCl)</td>
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<td>210.1</td>
<td>1.75(15)</td>
<td>104.51(5)</td>
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2. Synthesis of N-heterocyclic Carbene-Phosphinidene Adducts

The synthesis of N-heterocyclic carbene-phosphinidene adducts relies on the reaction of a suitable carbene or carbene precursor with the appropriate phosphorus source. This overview emphasizes the different methodologies to
access the NHC=PR adducts and is structured according to the phosphorus building blocks used.

1.2.1. Cyclopolyphosphines

In 1997, the first synthesis of an N-heterocyclic carbene-phosphinidene adduct using NHCs as starting material was reported by Arduengo and co-workers, who treated 1,3,4,5-tetramethylimidazol-2-ylidene (2) with pentaphenylcyclopentaphosphine (PPh)$_5$ at room temperature to afford 2·PPh ($\delta^{31}$P = −53.5) in 79% isolated yield (Scheme 2).$^3$ The upfield $^{31}$P NMR spectroscopy chemical shift proved to be characteristic for inversely polarized phosphaalkenes.$^{[5a]}$ The X-ray crystal structure of 2·PPh shows a central P–C bond of 1.794(3) Å and a N–C–P–R dihedral angle of 51.0(3)$^\circ$ between the imidazole ring and the P–C$_{Ph}$ bond, which indicates a weak P$_{px}$–C$_{pz}$ interaction. Arduengo and co-workers extended this approach to the sterically more hindered 1,3-dimesitylimidazol-2-ylidene (5) and obtained the corresponding adducts with phenylphosphinidene (5·PPh; $\delta^{31}$P = −23.0) and (trifluoromethyl)phosphinidene (5·PCF$_3$; $\delta^{31}$P = −23.6) in 67 and 90% yield, respectively (Scheme 2).$^{[19]}$

The larger N-substituent of 5 (versus 2) causes a downfield shift of the $^{31}$P NMR signal of 5·PPh, and in the solid state a reduced N–C–P–R dihedral angle of 26.5(7)$^\circ$, allowing $\pi$–$\pi$ stacking of the P-Ph and N-Mes rings. The related 5·PCF$_3$ displays similar values (P–C$_{NHC}$ 1.784(2) Å, N–C–P–R 31.3(2)$^\circ$; see Table 1).$^{[19]}$ In

\[ \text{Scheme 2. Synthesis of carbene-phosphinidene adducts from carbenes and cyclopolyphosphines.} \]
2013, Bertrand and co-workers showed that 1,3-di-iso-propylimidazol-2-yldene (3) can also be used and synthesized 3·PPh (79%, $\delta^{31}P = -61.2$; Scheme 2) in a similar fashion.$^{[15]}$

The groups of Slootweg and Grützmacher have extended this synthetic methodology by showing that carbenes can also be generated in situ, and synthesized 1·PPh, 5·PPh and 6·PPh from the corresponding imidazolium salts, (PPh)$_5$ and sodium tert-butoxide in an efficient one-pot synthesis in high yields (87–95%; Scheme 3).$^{[9]}$ 1·PPh ($\delta^{31}P = -49.1$; $P\cdots C_{NHC} 1.7917(14)$ Å, $N\cdots C\cdots P\cdots R$ 48.01(16)$^\circ$; see Table 1) displays features similar to the structurally related 2·PPh, both in solution and in the solid state.

![Scheme 3. One-pot synthesis of carbene-phenylphosphinidene adducts from imidazolium salts, (PPh)$_5$ and NaO$t$Bu.](image)

### 1.2.2. Diphosphenes

In analogy to the use of cyclopolyphosphines (RP)$_n$, also diphosphenes ($n = 2$), the smallest phosphinidene oligomer, can be applied in the synthesis of N-heterocyclic carbene-phosphinidene adducts. Matsuo and co-workers reacted the bulky diphosphenes (Rind)P=P(Rind) (Rind = 1,1,3,3,5,5,7,7-octa-R-substituted $s$-hydrindacen-4-yl; $R =$ Me, Et) with two equivalents of 1,3,4,5-tetramethylimidazol-2-yldene (2), which resulted in the quantitative formation of the NHC-phosphinidene adducts 2·P(EMind) ($\delta^{31}P = -70.5$) and 2·P(Eind) ($\delta^{31}P = -63.9$; Scheme 4).$^{[14]}$ The molecular structure of 2·P(Eind) shows that the coordinated NHC is almost perpendicular to the benzene ring of the Eind group with a central $P\cdots C$ bond of 1.767(3) Å and a $N\cdots C\cdots P\cdots R$ dihedral angle of 3.4(3)$^\circ$. 


Ragogna and co-workers discovered that the related phosphinidene selenides \((RP=Se)_n\) can be used as phosphorus source and treated the phosphinidene selenide dimer \((\text{DmpP}=\text{Se})_2\) (Dmp = 2,6-dimesitylphenyl) with 4 equivalents of 1,3,4,5-tetramethylimidazol-2-ylidene (2) or 1,3-di-iso-propyl-4,5-dimethylimidazol-2-ylidene (4) to afford the NHC=PR adducts \(2\cdot\text{P(Dmp)}\) \((\delta^{31}\text{P} = -76.7)\) and \(4\cdot\text{P(Dmp)}\) \((\delta^{31}\text{P} = -75.0)\) in 44 and 66% yield, respectively, together with the corresponding selenoureas (Scheme 5).\(^{[13]}\) The phosphinidene selenide trimer \((\text{DmpP}=\text{Se})_3\) works equally well as phosphinidene synthon and yields \(2\cdot\text{P(Dmp)}\).

\[\text{Scheme 5. Synthesis of carbene-phosphinidene adducts using the phosphinidene selenide dimer (DmpP=Se)_2. Dmp = 2,6-dimesitylphenyl.}\]

### 1.2.3. Chlorophosphines

NHC=PR adducts can also be prepared from carbenes and dichlorophosphines. Arduengo et al. showed that 2 equivalents of 1,3-dimesitylimidazolin-2-ylidene (10) react with dichlorophenylphosphine to afford
10·PPh ($\delta^{31}P = -10.4$) in 69% isolated yield after removal of the 2-chloro-1,3-dimesitylimidazolinium chloride byproduct by filtration (Scheme 6). The phosphorus chemical shift of 10·PPh is about 10 ppm downfield compared to 5·PPh which contains the analogous unsaturated NHC; however their solid state structures are rather similar (5·PPh: $P-C_{NHC} 1.763(6)$ Å, $N-C-P-R 26.5(7)^{\circ}$; 10·PPh: $P-C_{NHC} 1.746(4)$ Å, $N-C-P-R 19.5(5)^{\circ}$; see Table 1, section 3.3 and Scheme 26).

![Scheme 6. Preparation of carbene-phosphinidene adduct 10·Ph by carbene addition to phenyldichlorophosphine.](image)

Hudnall et al. modified Arduengo’s protocol to accommodate $\pi$-accepting carbonyl-decorated carbenes. They showed that treatment of PhPCl$_2$ with two equivalents of the carbenes 12–14 in the presence of trimethylsilyl triflate (1.0 equiv) afforded the adducts 12·PPh ($\delta^{31}P = 78.6$; $P-C_{NHC} 1.691(4)$ Å, $N-C-P-R 0.77^{\circ}$), 13·PPh ($\delta^{31}P = 37.7$) and 14·PPh ($\delta^{31}P = 83.0$; $P-C_{NHC} 1.726(3)$ Å, $N-C-P-R 9.83^{\circ}$) along with their 2-chloro-iminium triflate salts in modest yields (31.9–55.4%) (Scheme 7). Due to the increased $\pi$-acidity of these carbenes, the phosphorus atoms in 12–14·PPh resonate downfield, which is in accordance with their short P–C bond and near planar configuration as determined by single-crystal X-ray structure determinations and DFT calculations.
Scheme 7. Synthesis of carbonyl-decorated carbene-phosphinidene adducts from carbenes and PhPCl₂ in the presence of trimethylsilyl triflate (TMSOTf).

The generation of carbene-phosphinidene adducts can also be achieved using phosphorus trichloride. Roesky and co-workers reported the addition of PCl₃ to three different cyclic (alkyl)(amino)carbenes (CAACs; 2 equiv), which resulted in the formation of chlorophosphinidene adducts 19–21·PCI as mixtures of E- and Z-isomers concomitant with the formation of [CAACCICl]⁺Cl⁻ as by-product (Scheme 8).[31]

Scheme 8. Synthesis of CAAC-chlorophosphinidene adducts.

Bertrand and co-workers reported a general two-step procedure for making NHC=PR adducts from dichlorophosphines that requires only 1 equivalent of carbene. Namely, treatment of a large variety of carbenes with one equivalent of dichlorophenylphosphine results in the formation of the corresponding salts that,
after reduction (KC₈ or Mg) and subsequent work-up, afford the carbene-phosphinidene adducts (6, 9, 11, 13, 15–17, 21, 22)-PPh in 10–85% yield (Scheme 9; Table 1).[15]

Scheme 9. Bertrand’s two-step synthesis of NHC=PR adducts from carbenes and PhPCl₂ followed by reduction.

In a similar fashion cyclic (alkyl)(amino)carbene-phosphinidene adducts 21·P(N=SiPr) (δ³¹P = 134.0) [35] and 21·P(TMP) (δ³¹P = 135.4) [34] have been obtained (Scheme 10), which were subsequently used to generate phosphorus centered radical cations (see Section 1.4.1 and Scheme 31).

Furthermore, Robinson and co-workers have demonstrated that the reaction of PCl₃ with N-heterocyclic carbene 6 leads to adduct 6·PCl₃, which upon reduction with three equivalents of potassium graphite yields carbene-stabilized diphosphorus (6·P)₂ (56.6%; δ³¹P = −52.4), [36] and further reduction with Li metal afforded the anionic NHC–parent phosphinidene adduct Li-6·PH (16.3%; δ³¹P = −143.0; Scheme 11).[26] However, reduction of 6·PCl₃ with six equivalents of potassium graphite afforded the neutral 6·PH in 20% isolated yield (δ³¹P = −133.9; Scheme 11), as reported by Tamm et al.[23]
1.2.4. Phosphines

Tamm et al. described the use of tris(trimethylsilyl)phosphine as phosphorus source to access carbene-phosphinidene adducts. Treatment of \(N,N'-1,3\)-bis(2,6-
diisopropylphenyl)-2,2-difluorimidazoline ("PhenoFluor") with P(SiMe\(_3\))\(_3\) gives silylphosphinidene adduct 6·PSiMe\(_3\) (\(\delta^{31}\)P = −129.5) in 83% isolated yield, which upon methanolysis converts readily to the parent phosphinidene adduct 6·PH (\(\delta^{31}\)P = −133.8) in 81% yield (Scheme 12). Subsequently, 6·PSiMe\(_3\) was used for the synthesis of N-heterocyclic carbene–phosphinidyne transition metal complexes in analogy to the well-established imidazolin-2-iminato ligands (see Section 1.4.4 and Scheme 49).\(^{[23]}\)

![Scheme 12](image)

**Scheme 12.** Synthesis of NHC-phosphinidene adducts using P(SiMe\(_3\))\(_3\).

Primary phosphines follow a similar reaction course as the corresponding dichlorophosphines. Radius and co-workers showed that the reaction of one equivalent of phenylphosphine with two equivalents of 1,3-di-iso-propylimidazol-2-ylidene (3) leads to carbene-phosphinidene adduct 3·PPh (\(\delta^{31}\)P = −60.0) after 5 h at 105 °C in a quantitative yield next to the [3H\(_2\)] by-product (Scheme 13).\(^{[16]}\) When equimolar amounts of carbene and phosphine were used, also the cyclopolyphosphines (PPh)\(_4\), (PPh)\(_5\) and (PPh)\(_6\) were detected by \(^{31}\)P NMR spectroscopy. The NHC acts as a phosphine activator and hydrogen acceptor in these reactions.

Layfield and co-workers reported that in the presence of stoichiometric or catalytic amounts of [M(N(SiMe\(_3\))\(_2\))]\(_2\) (M = Fe, Co), N-heterocyclic carbenes 2, 5 and 6 react with phenyl or mesitylphosphines at 80 °C to give the carbene-phosphinidene adducts (2,5,6)-PPh and (2,5,6)-PMes (Scheme 13).\(^{[12]}\) The formation of 2-PMes is also catalyzed by the phosphinidene-bridged complex [(2)\(_2\)Fe(μ-PMes)]\(_2\), which provides evidence for metal-catalyzed phosphinidene transfer.
Phosphine gas (PH$_3$) can be employed to generate the corresponding NHC parent phosphinidene adducts. Grützmacher, Pringle and co-workers showed that in situ generated 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (11) inserts into the P–H bond of PH$_3$, giving access to phosphinyl–imidazolidine [11-H]-[PH$_2$], which upon dehydrogenation by 9,10-phenanthrenequinone yields the parent phosphinidene–carbene adduct 11·PH ($\delta^{31}$P = −116.7; Scheme 14).[29]
Chapter 1

1.2.5. Phosphides

Alternatively, 11·PH can be synthesized via the reaction between sodium tert-butoxide/sodium dihydrogenphosphide aggregate \{[Na(OtBu)]x[Na(PH2)]\} (x ≈ 2.5) and imidazolium chloride [11-H][Cl] followed by dehydrogenation (Scheme 14).\(^{[29]}\)

Interestingly, the first reported synthesis of N-heterocyclic carbene-phosphinidene adducts was also achieved using phosphides. In 1980, Schmidpeter and co-workers showed that carbene-cyanophosphinidene adducts 8·PCN (δ\(^{31}\)P = –133) and 18·PCN (δ\(^{31}\)P = –38) can be obtained by reacting [8-Cl][BF\(_4\)] and [18-Cl][BF\(_4\)] with [18]crown-6-sodium dicyanophosphide followed by reduction with sodium diethylphosphite (Scheme 15).\(^{[4]}\) The X-ray crystal structure of 8·PCN shows a central P–C bond of 1.771(5) Å and that the two moieties (PCN and N-heterocycle) are not coplanar, which indicates a weak P\(_{π}–\)C\(_{π}\) interaction. At the time, these adducts were not recognized as carbene-phosphinidene adducts, although they clearly belong to this class of compounds.

![Scheme 15. Synthesis of carbene-cyanophosphinidene adducts from sodium dicyanophosphide.](image)

Another effective route to NHC-phosphinidene adducts was developed by Grützmacher and co-workers, who employed sodium phosphaethynolate, Na(OCP), as a phosphorus atom transfer reagent. Treatment of the N-arylated imidazolium salt [6-H][Cl] with Na(OCP) for 4 hours in refluxing THF afforded after
work-up $6 \cdot \text{PH} \ (\delta^{31}P = -136.7)$ in 71% yield (Scheme 16). Analogously, the parent phosphinidene adducts $7 \cdot \text{PH} \ (87\% ; \ \delta^{31}P = -134.5)$ and $10 \cdot \text{PH} \ (34.5\% ; \ \delta^{31}P = -127.2)$ were prepared (Scheme 16), yet this method does not tolerate N-alkylated imidazolium salts, such as $[1-\text{H}][\text{Cl}]$ and $[3-\text{H}][\text{Cl}]$. 

![Scheme 16. Synthesis of carbene-phosphinidene adducts by phosphide transfer reactions from Na(OCP).](image)

### 1.2.6. Phosphaketenes

For the synthesis of substituted phosphinidene adducts, Na(OCP) can also be used to prepare tetrel substituted phosphaketenes, such as $\text{Ph}_3\text{Sn}(\text{PCO})$ and $\text{Ph}_3\text{Ge}(\text{PCO})$. These phosphaketenes react with NHCs $5$, $6$ and $11$ to form the corresponding NHC-phosphaketene adducts that decompose upon thermolysis under the release of carbon monoxide to afford NHC-phosphinidene adducts $(5, 6, 11) \cdot \text{PEPh}_3 \ (E = \text{Sn}, \text{Ge})$ almost quantitatively (Scheme 17).
Scheme 17. Carbene-phosphinidene adduct synthesis from NHC-phosphaketene adducts.

1.2.7. Phosphinidenes

Sterically encumbered phosphaketenes can also be decarbonylated prior to the addition of N-heterocyclic carbenes. Bertrand and co-workers have isolated a room-temperature stable, monomeric (phosphino)phosphinidene (P(DAP)), by photolysis of the corresponding (phosphino)phosphaketene (OCP(DAP)) (Scheme 18). Its isolation opened a novel avenue towards NHC-phosphinidene adducts, simply by phosphinidene addition to carbenes. In this fashion, the phosphinidene adducts of CAAC 20 (20·P(DAP); $\delta^{31}P = 76.3$) and less electrophilic carbenes such as imidazol-2-ylidene 3 (3·P(DAP); $\delta^{31}P = -68.2$) and benzimidazol-2-ylidene 9 (9·P(DAP); $\delta^{31}P = -35.5$) have been prepared (Scheme 18), illustrating the electrophilic nature of this phosphinidene.$^{[17]}$
Scheme 18. Synthesis of carbene-phosphinidene adducts by phosphinidene addition to carbenes. DAP = 1,3-bis-Ar-1,3,2-diaza phospholidine.

1.2.8. Phosphinidene Transfer

For thermally unstable phosphinidenes, Driess and co-workers developed a phosphinidene transfer reaction. Phosphasilene 23·PH ($\delta^{31}P = -293.9$) features a highly polarized Si–P bond, which enables transfer of the parent phosphinidene, [PH], at room temperature to N-heterocyclic carbene 6 to quantitatively afford 6·PH ($\delta^{31}P = -136.7$) and silylene 23 (Scheme 19).

Scheme 19. Synthesis of parent carbene-phosphinidene adduct 6·PH by phosphinidene transfer.
1.2.9. Phosphaalkynes

The only example of using phosphaalkynes to produce NHC-phosphinidene adducts comes from Hahn et al., who synthesized the bicyclic adduct (2-H)-PCHN(iPr)_2 (δ^{31}P = -64.8) in almost quantitative yield from aminophosphaalkyne iPr_2NCP and N-heterocyclic carbene 2 (Scheme 20).\textsuperscript{[11]} To date, this remains the only example of an intramolecular carbene-stabilized phosphinidene.

\[
\text{Scheme 20. Synthesis of the intramolecular carbene-stabilized phosphinidene adduct (2-H)-PCHN(iPr)_2 from a phosphaalkyne and 2.}
\]

1.2.10. Polyphosphorus compounds

Next to monophosphorus building blocks, polyphosphorus compounds have also shown their utility as the parent phosphinidene adducts of carbenes have been found to be equally well accessible from elemental phosphorus and polyphosphides, although not all phosphorus atoms of the starting material are incorporated into the product. In 2016, the groups of Grützmacher and Gudat reported on the reactions of elemental phosphorus (P_4) with \textit{in situ} generated carbenes, from imidazolium salts and KOtBu, to produce (1, 2, 5, 6)-PH adducts together with bis(NHC)-stabilized phosphorus cations and some unidentified polyphosphorus compounds (Scheme 21).\textsuperscript{[8]} Soon after, Lammertsma, Slootweg and co-workers have demonstrated that 6-PH can also be prepared from white phosphorus in two controllable steps. First, P_4 was functionalized with the bulky Mes^*Li (Mes^* = 2,4,6-tBu_3C_6H_2) and BPh_3 to give the borane-stabilized bicyclo[1.1.0]tetraphosphabutane anion Mes^*P_4^-, which through selective [3+1] fragmentation using imidazolium chloride [6-H][Cl] afforded 6-PH, while the P_3-unit was trapped with 1,3-cyclohexadiene (Scheme 21).\textsuperscript{[40]}

34
Scheme 21. Preparation of carbene-phosphinidene adducts from elemental phosphorus. X = Cl or I, Mes* = 2,4,6-\text{tBu}_3C_6H_2, CHD = cyclohexadiene.

The heptaphosphides Na$_3$P$_7$ and (Me$_3$Si)$_3$P$_7$ can be easily obtained from P$_4$ and P$_{\text{red}}$, and are versatile precursors for the synthesis of carbene-phosphinidene adducts.$^8$ Grützmacher and co-workers demonstrated that (dihydro)imidazolium chlorides react with Na$_3$P$_7$\textsuperscript{[8]} or (Me$_3$Si)$_3$P$_7$\textsuperscript{[22,29]} resulting in phosphinidene adducts of both unsaturated (1, 3, 5, 6) and saturated (11) carbenes with varying steric demand in high yields (Scheme 22).

Scheme 22. Synthesis of NHC=PH adducts from heptaphosphides.

In 2016, Hey-Hawkins and co-workers illustrated that sodium tetramesityltetraphosphinediide (Na$_2$(THF)$_4$P$_4$Mes$_4$) is a convenient precursor for
mesitylphosphinidene adducts. Treating Na$_2$(THF)$_4$P$_4$Mes$_4$ with two equivalents of 1,3-dimethylimidazol-2-ylidene (1) or the corresponding imidazolium iodide [1-H][I] gave mesitylphosphinidene adduct 1·PMes in 68% yield ($\delta^{31}$P = –73.8; Scheme 23).[10]

![Scheme 23. Synthesis of 1·PMes from Na$_2$(THF)$_4$P$_4$Mes$_4$.](image)

### 1.3. Structure and Bonding

In this part, an overview is provided of the reports describing the nature of the central P–C bond of N-heterocyclic carbene-phosphinidene adducts analyzed by DFT calculations, NMR spectroscopy, as well as single-crystal X-ray crystallography.

#### 1.3.1. Theoretical Studies

Generally, the electronic properties of C-amino substituted phosphaalkenes differ significantly from the classical C-substituted phosphaalkenes R$_1$R$_2$C=PR$_3$. Due to the presence of $\pi$-electron-donating nitrogen atom(s) adjacent to the carbenic carbon, which enables delocalization of the nitrogen lone pair to the central PC bond, the polarity of the P=C bond is reversed (P$^{\delta–}$–C$^{\delta+}$).[5a] To analyze this bonding situation in the adducts of the parent phosphinidene, PH, with the parent imidazol-2-ylidene (I) and imidazolin-2-ylidene (II; Scheme 24),[41] Frison and Sevin have used charge decomposition analysis (CDA). This showed these adducts display strong $\sigma$-donation of the in-plane NHC lone pair to the phosphinidene moiety, in combination with $\pi$-back bonding of the phosphinidene moiety to the carbene, creating partial double-bond character of the C–P unit.
The double bond character in II-PH is more pronounced due to stronger $\pi$-back donation of the phosphinidene moiety; the reduced $\pi$-back bonding in I-PH stems from delocalization of the nitrogen lone pairs that contribute to the ring aromaticity of the imidazol-2-ylidene.$^{[41a]}$

![Scheme 24. Model compounds used for DFT calculations by Frison and Sevin.](image)

![Scheme 25. Schematic representation of the dominant orbital interactions forming the central C–P bond.](image)

The phosphorus substituent can have a steric effect on the geometry of the carbene-phosphinidene adducts, resulting in loss of planarity of the NHC=PR core indicated by the increased N–C–P–R dihedral angle between the imidazole ring and the P–R bond that weakens the P$_{\pi}$–C$_{\pi}$ interaction. Investigation of electronic effects showed that electron-withdrawing substituents lower the double-bond character of the C–P bond, while electron-donating groups have an opposite effect.$^{[41c]}$ Roesky and co-workers have used energy decomposition analysis (EDA) to determine whether the P=C double bond of CAAC-phosphinidene adducts originates from $\sigma$ donation P$\leftarrow$C and $\pi$ back-donation P$\rightarrow$C between two closed-shell fragments or is formed via classical electron-sharing between two triplet fragments. By comparing orbital interaction term ($\Delta E_{orb}$) for the corresponding singlet and triplet fragments, it was shown that 19-P(SiL) may equally well be
described with dative bonds as well as with a classical double bond, while \( 19 \cdot P(SiCl_2L) \) features a classical double bond.\[33\]

Several other computational studies on NHC-phosphinidene adducts confirmed that polarization of the P–C π-bond is highly dependent on the nature of the carbene as well as the phosphinidene. Tamm and co-workers have performed an NBO analysis of imidazol-2-ylidene adduct \( 6 \cdot PPh \) and found that the P–C π-bond is significantly polarized towards phosphorus (60.7%), while the σ-bond is polarized towards the carbene carbon (66.5%).\[24\] The anionic NHC–parent phosphinidene adduct Li-I-PH features an even more P-localized P–C π-bond (71.2% P and 28.5% C) and C-localized σ-bond (65.7% C and 34.3% P).\[26\] Phosphinidene adducts of monoamidocarbene \( 13 \cdot PPh \) and CAACs \( 21 \cdot PPh, \[30\] E-19-PCl\[31\] and \( 19 \cdot P(SiL)\[33\] also feature P-polarized π-bonds (60.0%, 60.3%, 59.5% and 59.0% at P, respectively). In contrast, diamidocarbene-phenylphosphinidene adducts \( 12 \cdot PPh \) and \( 14 \cdot PPh\[30\] and Z-isomer of CAAC-chlorophosphinidene adduct \( Z-19-PCl\[31\] are characterized by a more developed π-bond which is equally localized at the P (52.9%, 53.7% and 53.2%, respectively) and C (47.1%, 46.3% and 46.8%) atoms, leading to a higher contribution of the phosphaalkene resonance structure A (). Additionally, the Wiberg bond indexes (WBI) indicate that \( 12 \cdot PPh, \ 14 \cdot PPh \) (WBI for the P atom, including two σ and one π-bond, are 2.91 and 2.90)\[30\] and \( Z-19-PCl \) (WBI of the P–C bond is 1.626)\[31\] have a higher double-bond character than \( 19 \cdot P(SiL), \ 19 \cdot P(SiCl_2L), \[33\] 6·PH\[21\] and \( E-19-PCl\[31\] (WBI of the P–C bond are 1.57, 1.55, 1.36 and 1.535, respectively).

1.3.2. NMR spectroscopy

As a result of the inverse polarization of the PC bond in N-heterocyclic carbene-phosphinidene adducts, the phosphorus atom is electron-rich (in agreement with resonance forms B and C; Scheme 1), which results in upfield \( ^{31}P \) NMR chemical shifts (between \( \delta^{31}P = -179.5 \) ppm for \( 5 \cdot PSnPh_3 \[20\] and \( \delta = 163.4 \) ppm for \( E-21-PCl\[31\] see Table 1), compared to those of classical phosphaalkenes (\( \delta^{31}P = 230–420 \) ppm).\[42\] For NHC=PPh adducts, Bertrand and co-workers showed
that the $^{31}$P NMR chemical shifts can be used as indicator to evaluate the relative
$\pi$-accepting properties of carbenes.$^{[15]}$ More $\pi$-accepting carbenes induce stronger
$\pi$-back donation from the phosphinidene moiety to the carbene (increasing the
contribution of resonance form A that features a formal P=C double bond; Scheme
1). As a result, the phosphorus atom becomes more electron-poor and its $^{31}$P NMR
chemical shift more downfield. For example, the increased $\pi$-accepting capability of
the saturated NHCs (10 and 11) compared to their unsaturated analogues (5 and
6) is reflected in more downfield $^{31}$P NMR shifts for 10·PPh and 11·PPh (−10.4 and
−10.2 ppm) versus 5·PPh and 6·PPh (−23.0 and −18.9 ppm), which corresponds
with the theoretical studies discussed in 1.3.1.

$^1$H and $^{13}$C NMR spectra also reflect the nature of the PC bond, as greater
double bond character increases the rotational barrier around the PC bond, which
makes the N-substituents inequivalent on the NMR time scale. 6·PPh shows one
set of sharp signals corresponding to equivalent Dipp (Dipp = diisopropylphenyl)
groups in both $^1$H and $^{13}$C NMR spectra at room temperature indicating facile
rotation around the PC bond, while 11·PPh bearing the more $\pi$-accepting saturated
NHC displays broad signals caused by a hampered rotation around the more
pronounced P=C bond. VT NMR studies confirm the difference in enthalpy of
activation for the rotation process, namely $\Delta G^\ddagger = 34$ kJ mol$^{-1}$ for 6·PPh and $\Delta G^\ddagger = 58$
kJ mol$^{-1}$ for 11·PPh.$^{[15]}$ Furthermore, the (12–14)·PPh adducts bearing the strongly $\pi$-accepting carbonyl-decorated carbenes 12–14 exhibit more downfield
$^{31}$P NMR shifts, compared to the analogous adducts 10·PPh and 15·PPh that lack
the carbonyl groups, confirming their significant multiple P–C bond character, which
is also indicated by the inequivalent mesityl groups displayed in the $^1$H and $^{13}$C
NMR spectra in solution at room temperature.$^{[30]}$

The nature of the phosphorus substituent on the NHC=PR adducts also has a
significant influence on the $^{31}$P chemical shift. As predicted by DFT calculations,$^{[41c]}
electron-withdrawing substituents (e.g., Ph, Mes) result in more downfield $^{31}$P NMR
shifts, whereas electron-donating groups (e.g., SiMe$_3$, GePh$_3$, SnPh$_3$) lead to more
upfield shifts. Indeed, the $^{31}$P NMR chemical shifts of 6·PPh (−18.9 ppm) and
6·PMes (−52.1 ppm) are more downfield than the corresponding 6·PH (−134.3 ppm), while adducts with electron-donating groups, like 6·PGePh₃ (−145.1 ppm) and 6·PSnPh₃ (−161.5 ppm), have more upfield shifts. This is in agreement with decreasing electron-withdrawing ability in the series Ph > Mes > H > GePh₃ > SnPh₃.

Another important factor influencing the ³¹P NMR chemical shift is the stereochemistry around the P=C bond. For amino-substituted phosphaalkenes (phosphaamidenes) it was found that the E-isomers display more downfield ³¹P NMR chemical shifts than the Z-isomers.[⁴³,⁷ᵃ] This also holds true for the NHC=PR adducts, where the ³¹P NMR shift of the E-configured adduct 21·PPh is more downfield (δ = 68.9 ppm) than the signal of the related adduct 22·PPh (δ = 56.2 ppm) with a Z-configuration.[¹⁵] Furthermore, Roesky and co-workers have characterized isomeric pairs (E and Z isomers) of 19·PCI, 20·PCI and 21·PCI and found that in all cases the E-isomers exhibit more downfield chemical shifts (δ³¹P = 160.3–163.4 ppm) than the corresponding Z-isomers (δ³¹P = 129.4–135.0 ppm).[³¹]

The ¹³C NMR chemical shifts of the carbene carbon of the NHC-phosphinidene adducts follow the same trend, albeit less pronounced (166.8–219.4 ppm; Table 1).

1.3.3. Single-crystal X-ray crystallography

The most noticeable structural features of NHC=PR adducts reflecting the nature of the PC bond are the P−C bond distance, the C−P−R bond angle and N−C−P−R dihedral angle between the imidazole ring and the P−R bond (see Table 1). The P−C bond lengths of the NHC=PR adducts are elongated compared to classical phosphaalkenes (1.65–1.67 Å) and vary between 1.691(4) Å for 12·PPh and 1.799(3) Å for 4·P(Dmp). As expected, greater π-acidity of the carbene (e.g., 12) leads to a shorter P−C bond, while weakly π-accepting carbenes (e.g., 4) display elongated P−C bonds. Moreover, the degree of PC double bond character also impacts the C−P−R bond angle. In the case of reduced π-back donation, the substituent on phosphorus can freely twist out of the carbene plane (e.g. 5·PPh, N−
C–P–C(Ph) 26.5(7)°, without impacting the valence angle at P (99.9(3)°) which remains similar to the that of parent phosphinidene adduct (5·PH, 100(2)°). In contrast, adduct 12·PPh that bears the same N (Mes) and P (Ph) substituents, but a more \( \pi \)-accepting carbene, has a shorter P–C bond. This prevents twisting of the Ph-group out of the carbene plane (N–C–P–C(Ph) 0.77°) and, consequently, the C–P–R bond angle increases (106.65(17)°) to relieve steric strain. These examples demonstrate that the planar adduct 12·PPh has a higher contribution of resonance form A, while adducts 4·PPh and 5·PPh favor resonance structures B/C; and 10·PPh has an intermediary position (Scheme 26).

Scheme 26. Influence of carbene \( \pi \)-acidity on the \( ^{31} \text{P} \) NMR chemical shift and selected structural parameters of NHC-phosphinidene adducts with the same P substituent.

1.4. Reactivity of N-heterocyclic Carbene-Phosphinidene Adducts

N-Heterocyclic carbene phosphinidene adducts can undergo a variety of reactions that all have been discovered in recent years. This overview of the reactivity of NHC=PR adducts is structured as follows: 1) addition reactions with main-group and organic compounds, 2) substitution reactions with main-group and organic compounds, 3) addition reactions with transition-metal complexes, 4)
substitution reactions with transition-metal complexes, and 5) phosphinidene transfer reactions by cleavage of the central C–P bond.

1.4.1. Addition reactions with main-group and organic compounds

Reactions with group 13 electrophiles. In their seminal work on NHC-phosphinidene adducts, Arduengo and co-workers investigated the reactivity of 5·PPh towards boron trihydride to illustrate the availability of two lone pairs on phosphorus. The reaction of 5·PPh ($\delta^{31}P = -23.0$) with two equivalents of BH$_3$·THF resulted exclusively in bis(borane) adduct 24 (73%, $\delta^{31}P = 4.0$; Scheme 27) that displays an elongated C–P bond in the solid state (1.856(2) Å) compared to 5·PPh (1.763(6) Å), indicating a decrease in bond order.$^{[44]}$ Interestingly, the more sterically demanding Lewis acid BPh$_3$ induces formation of cyclopolyphosphines (PPh)$_n$, ($n = 3$–5; Scheme 27), which preludes the possibility of developing phosphinidene transfer reactions (see 1.4.5). The BH$_3$ groups could be removed with 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) and 1,5-diazabicyclo[4,3,0]non-5-ene (DBN) in a competition experiment, but not with the less basic phosphine PAr$_3$ (Ar = C$_6$H$_2$(OMe)$_3$-2,4,6). Arduengo et al. also probed for the first time the redox chemistry of NHC=PR adducts by means of cyclic voltammetry and established that 5·PPh undergoes facile one-electron oxidation at –0.08 V (vs. SCE).

\[
\begin{align*}
(PPh)_n & \quad \text{BPh}_3 \quad \text{Mes} \quad \text{Ph} \quad \text{N} \quad \text{N} \quad \text{P} \quad \text{Ph} \quad \text{Mes} \quad \text{P} \quad \text{BH}_3 \quad \text{Mes} \quad \text{Mes} \\
& \quad \text{NHC·BPh}_3 \\
& \quad n = 3–5 \\
\end{align*}
\]

Scheme 27. Reactions of 5·PPh with BH$_3$ and BPh$_3$.

Following a similar protocol, the groups of von Hänisch, Bertrand and Hahn showed that, respectively, 5·PH$_2$,$^{[18]}$ 7·PH$_2$,$^{[27]}$ and (2-H)·PCHN(iPr)$_2$,$^{[11]}$ react with two equivalents of BH$_3$·THF or BH$_3$·SMe$_2$ to form the corresponding bis(borane) adducts 25, 26 and 30 (Scheme 28 and Scheme 32).
Ragonna and co-workers reacted 4·P(Dmp) ($\delta^{31}P = -75.0$) with the strongly Lewis acidic B(C$_6$F$_5$)$_3$ in THF, which results in controlled ring-opening of THF affording product 27 ($\delta^{31}P = -24.7$; Scheme 29).

In contrast to the parent borane, treatment of 10·PH ($\delta^{31}P = -127.2$) with the bulkier Lewis acids $t$Bu$_2$AlCl and $t$Bu$_2$GaCl gave mono(alane) and mono(galane) adducts 28 ($\delta^{31}P = -151.0$) and 29 ($\delta^{31}P = -148.8$; Scheme 30). The increased shielding of the phosphorus nucleus in these compounds indicates an enhanced polarization of the central C–P bond, which is in accordance with the elongated C–P bonds observed in the solid state (1.801(2) Å (28) and 1.798(2) Å (29) vs. 1.7464(16) Å for 10·PH).
**Oxidation.** Stimulated by Arduengo’s earlier results, Bertrand and co-workers investigated the redox chemistry of CAAC-phosphinidene adducts \(21 \cdot P(TMP)^{[34]}\) and \(21 \cdot P(N=SI\text{Pr})^{[35]}\) with \([\text{Ph}_3C][(C_6F_5)_4B]\), which resulted in one-electron oxidation affording the thermally stable radical cations \(21 \cdot P(TMP)^{+}\) and \(21 \cdot P(N=SI\text{Pr})^{+}\) that display significant spin density on the phosphorus atom (0.67 e and 0.40 e, respectively), as determined by DFT calculations. Addition of KC\(_8\) to a toluene solution of \(21 \cdot P(N=SI\text{Pr})^{+}\) resulted in reformation of the neutral \(21 \cdot P(N=SI\text{Pr})\) by one-electron reduction, thus illustrating a fully reversible redox system (Scheme 31).\(^{[35]}\)

![Scheme 31. Redox chemistry of CAAC-phosphinidene adducts.](image)

Hahn and co-workers applied oxygen from air as oxidant serendipitously. Namely, upon exposure of NHC-phosphinidene adduct (2-H)-PCHN(iPr)\(_2\) (\(\delta^{31}P = -64.8\)) in benzene to air for several weeks a small amount of bis(oxide) \(31\) (\(\delta^{31}P = 90.5\)) was obtained and crystallographically characterized (Scheme 32).\(^{[11]}\)
Scheme 32. Reactions of (2-H)-PCHN(iPr)_2 with BH_3 and air.

To date no NHC-stabilized mono(phosphinidene)oxides have been reported, yet the related base-stabilized phosphinidene sulfide became very recently available. Ragogna and co-workers treated the dimeric phosphinidene sulfide (DmpP=S)_2 (δ_31P = 124) with two equivalents of 1,3-di-iso-propyl-4,5-dimethylimidazol-2-ylidene (4) at room temperature to afford the first monomeric phosphinidene sulfide 4·P(S)Dmp (δ_31P = 29; Scheme 33).[45]

Scheme 33. Synthesis of a NHC-stabilized phosphinidene sulfide.

Protonation and alkylation. Next to neutral Lewis acids and oxidants, the reactivity of NHC=PR adducts has also been studied towards cationic electrophiles. Bertrand and co-workers have demonstrated that the sterically encumbered parent phosphinidene adduct 7·PH can be protonated and alkylated at the phosphorus atom. Addition of trifluoromethanesulfonic acid (HOTf) to a benzene solution of 7·PH (δ_31P = −134.5) afforded the NHC-stabilized parent phosphonium salt 32 (85%, δ_31P = −166.6; Scheme 34), while alkylation was achieved by treatment of 7·PH with methyl trifluoromethanesulfonate (MeOTf) and [Ph_3C][BF_4] resulting in
NHC-stabilized phosphonium salts 33 (87%, \(\delta^{31}P = -86.3\)) and 34 (89%, \(\delta^{31}P = -49.4\)), respectively (Scheme 34).\(^{[27]}\)

![Scheme 34. Protonation and alkylation reactions of 7-PH.](image)

1.4.2. Substitution reactions with main-group and organic compounds

Apart from functioning as a strong Lewis base (see Section 1.4.1), PH- and PCl-functionalized N-heterocyclic carbene phosphinidene adducts can also undergo substitution reactions at the phosphorus center offering an alternative approach to create functionalized NHC=PR adducts. For example, Grützmacher and co-workers showed that the parent phosphinidene-carbene adduct 6-PH (\(\delta^{31}P = -136.7\)) reacts with dichlorophosphines PCl\(_2\)R in the presence of the non-nucleophilic base DABCO (1,4-diazabicyclo[2.2.2]octane) to yield the neutral species 6·PPCl\(_R\) (\(R = \text{Ph (a) } \delta^{31}P = -17.3\) or \(\text{NiPr}_2 (b) \delta^{31}P = -18.4\); see Scheme 35).\(^{[25]}\) However, treatment of 6-PH with chlorobis(dimethylamino)phosphine does not afford 6·PP(NMe\(_2\))\(_2\), but 6·PPCINMe\(_2\) \(35c (\delta^{31}P = -33.5)\) and P(NMe\(_2\))\(_3\) as a second equivalent of PCl(NMe\(_2\))\(_2\) acts as chloride donor (Scheme 35).\(^{[25]}\) The pnictogen chlorides ECl\(_3\) (0.5 equiv; E = P, As) also react with 6-PH in the presence of DABCO, but now spontaneous dissociation of the P–Cl bond occurs to afford the carbene-supported P\(_3\) and PAsP cations 36 (\(\delta^{31}P = 190.6 (P=C), 591.9\)) and 37 (\(\delta^{31}P = 218.9\)) (Scheme 35).\(^{[22]}\) Further reactions of 36 and 37 with magnesium metal led to the reduction of both compounds into the
neutral radicals 38 and 39. Moreover, phosphorus radical 38 was able to undergo a [3+2] cycloaddition to formally result in P₃ transfer (see Section 1.4.5 and Scheme 51).[22]

![Scheme 35. Reactions of 6·PH with pnictogen chlorides. DABCO = 1,4-diazabicyclo[2.2.2]octane.](image)

Chlorophosphines 35 offer interesting follow-up chemistry. Namely, treatment of 35 with gallium trichloride resulted in chloride abstraction and the formation of the corresponding cationic diphosphenes [6·P=PR]+ 40, which depending on the steric bulk of the R substituent are either monomeric (40b) or dimerize via [2+2] cycloaddition to afford the dicationic cyclotetraphosphines 41a,c. The high P–P double bond character in 40 has also been evidenced from hetero-Diels-Alder reactions with 2,3-dimethylbuta-1,3-diene and cyclopentadiene, resulting in the cationic 1,2-diphosphinanes 42 and 43 (Scheme 36).[25]
Scheme 36. Chloride abstraction reactions of 35 with GaCl₃ both in the presence and absence of trapping agents.

Hänisch and co-workers demonstrated that the saturated NHC phosphinidene adduct 10·PH can be deprotonated using benzyl potassium resulting in NHC–phosphinidenyl 10·PK, which can be functionalized with tBu₂MCl (M = Al, Ga) affording aluminum and gallium phosphinidenyl complexes 44–46 (Scheme 37).

Frenking, Stalke, Roesky and co-workers have reported on the functionalization of chlorophosphinidene adduct 19·PCI (δ³¹P = 161.9/129.4), which oxidatively adds to chlorosilylene LSiCl (L = benzamidinate) affording dichlorosilane 19·PSiCl₂L (84%, δ³¹P = 59.0) that upon reduction with two equivalents of potassium graphite generated the CAAC-stabilized silylene-phosphinidene 19·PSiL (67%, δ³¹P = 68.8; Scheme 38).

Reduction of chlorophosphinidene adduct 19·PCI with LiAlH₄ affords the parent phosphinidene-CAAC adduct 19·PH (70%, δ³¹P = −38.4/−44.9), which upon lithiation with MeLi in THF gives lithium phosphinidenyl [19·PLi(THF)]₂ (65%, δ³¹P = 177.3; Scheme 38).
Scheme 37. Synthesis of aluminium(III) and gallium(III) phosphinidenyl complexes. Bn = benzyl, NHC = 10.

Scheme 38. Follow-up chemistry of chlorophosphinidene adduct 19-PCI.

Lithium phosphinidenyl [19-PLi(THF)$_2$]$_2$ can be considered as a monoanionic phosphorus atom stabilized by CAAC and was used as a precursor for the synthesis of various base-stabilized phosphinidenes containing P–C (19·P($\rho$-C$_6$F$_4$N) (47; 71%, $\delta^{31}$P = -4.3), 19·PnBu (48; 79%, $\delta^{31}$P = 61.2), 19·P($\alpha$-Py) (54; 68%, $\delta^{31}$P = 65.4)), P–Si (19·PSiCl$_3$ (49; 67%, $\delta^{31}$P = -22.0), P–Ge (19·PGeCl$_3$ (50;
85%, $\delta^{31}\text{P} = 47.8)$) and P-P bonds (19·PPCl$_2$ (51; 76%, $\delta^{31}\text{P} = 242.5, 73.9$), 19·PPCl(Cy) (52; 75%, $\delta^{31}\text{P} = 135.8, 53.5$), 19·PPPh$_2$ (53; 80%, $\delta^{31}\text{P} = 41.2, -27.3$; see Scheme 39).\cite{32}

\[ \text{Scheme 39. Reactions of base-stabilized phosphorus atom with organic and inorganic substrates. Cy = Cyclohexyl.} \]

\subsection*{1.4.3. Addition reactions with transition-metal complexes}

N-Heterocyclic carbene-phosphinidene adducts have been treated with a variety of transition-metal complexes leading to, in analogy to the main-group based Lewis acids, $\eta^1$-coordination to either one or both of the available lone pairs at the phosphorus site (see 1.4.1). The first study exploring the coordination chemistry of NHC=PR adducts towards transition metals was reported by Larocque
and Lavoie in 2014, who reacted 5-PPh with Grubbs first-generation ruthenium benzylidene complexes. Addition of 5-PPh (1 equiv) to RuCl$_2$(PPh$_3$)$_2$(CHPh) resulted in ligand exchange and the formation of $\eta^1$-coordination product 55, which was, however, inactive in ring-opening metathesis of diallyl sulfide. The use of RuCl$_2$(PCy$_3$)$_2$(CHPh) did not afford RuCl$_2$(5-PPh)(PCy$_3$)(CHPh), but led instead to complex 56, which is formed via two consecutive C–H activation steps (Scheme 40).

**Scheme 40.** Reactions of 5-PPh with the first-generation Grubbs’ catalyst and various coinage metal complexes.

Dias and co-workers explored the coordination chemistry of 5-PPh towards coinage metals and prepared the bimetallic coinage metal complexes 57 (Scheme 40). While copper(I) and silver(I) adducts 57a–c crystallized as halide ion bridged octanuclear complexes, bis-gold(I) chloride adduct 57d remained monomeric in the solid state. Similarly, coinage metal complexes 58–60 of Dipp-substituted analogue 6-PPh were obtained by Tamm and co-workers (Scheme 41). Depending on the stoichiometry of the reactions with CuCl and AuCl(SMe$_2$), monometallic 58a,c or bimetallic complexes 59a,c were isolated, indicating the possibility of the stepwise complexation of the P moiety. The reaction of 6-PPh with AgCl afforded only monometallic complex 58b, while the reaction with CuOTf resulted exclusively in...
bis-copper complex 60 (Scheme 41). In contrast to 57a–c, complexes 58–60 are monomeric in the solid state, likely due to the bulkier Dipp-groups (versus the Mes-groups in 57), which prevent oligomerization through M–P–M or M–Cl–M bridges.

Scheme 41. Synthesis of coinage metal complexes of 6·PPh.

Subsequent treatment of the bimetallic complexes 59 (M = Cu, Au) with chloride abstraction reagents (NaBArF$_{24}$ or AgSbF$_{6}$) gave the dicaticionic tetranuclear complexes 61, which feature a remarkable central eight-membered ring bearing short Cu···Cu and Au···Au distances, respectively, along the chlorine-bridged metal–metal axes (Scheme 42).$^{[24]}$ Complete chloride abstraction was observed by reacting 59c with two equivalents of AgSbF$_{6}$ in the presence of tetrahydrothiophene (tht), which afforded complex 62. Both gold species 61 and 62 were employed as catalysts for 1,6-enzyme cyclization and carbene transfer reactions using diethyl diazoacetate, thereby illustrating for the first time the application of NHC-phosphinidene complexes in homogeneous catalysis.
Ragogna and co-workers explored the coordination of (tht)AuCl to 4·P(Dmp) ($\delta^{31}P = -75.0$). This reaction resulted in the formation of bis-gold(I) chloride complex 63 ($\delta^{31}P = -41.9$; Scheme 43) which akin to 59c is monomeric in the solid state.\[13\]

Bertrand and co-workers have demonstrated that also the parent carbene-phosphinidene adduct 7·PH reacts with two equivalents of (tht)AuCl resulting in bis-metal complex 64 (Scheme 44).\[27\] In contrast, treatment of 7·PH with diiron nonacarbonyl led to mono-iron complex 65, due to steric constraints as the addition of excess [Fe$_2$(CO)$_9$] did not lead to further coordination.
To probe the P-donor properties of the NHC=PR adducts, Tamm and co-workers reacted 6·PR (R = H, Ph, Mes) with the metal carbonyl complexes [Rh(µ-Cl)(CO)₂]₂, [W(CO)₅(NMe₃)] and [Mo(CO)₅(THF)] to afford dicarbonyl rhodium(I) complex 66, tetraneuclear complex 67, and tungsten and molybdenum pentacarbonyl complexes 68 (M = Mo, W), respectively (Scheme 45). IR spectroscopic analysis of the CO stretching frequencies of 66 and 68 revealed the much stronger electron-donating ability of the carbene-phosphinidene adducts 6·PR, when compared to phosphines and NHCs. Values similar to those of the related carbodicarbenes, also bearing two lone pairs on the donor atom, were observed.

NHC=PR carbonyl complexes 69 of the group 6 transition metals can also be prepared directly from the metal hexacarbonyls [M(CO)₆] (M = W, Mo, Cr) using UV light, as was shown by Bispinghoff and Grützmacher for 6·PH (Scheme 45). Using parent phosphinidene adduct 5·PH that bears the less hindered 1,3-dimesitylimidazol-2-ylidene (5) even the bimetallic carbonyl complex could be detected. Thus, addition of one equivalent of [W(CO)₅(THF)] to 5·PH afforded monometallic 70, which upon addition of an excess of [W(CO)₅(THF)] led to a mixture of 70 and bimetallic 71 that was spectroscopically characterized (Scheme 46). Interestingly, these carbonyl complexes mimic carbene adducts of the
transient electrophilic phosphinidenes [RP=M(CO)₅], such as [(2-PR)W(CO)₅] (R = CH(SiMe₃)₂) that was prepared by Streubel and co-workers.\textsuperscript{[50]}

![Scheme 45](image.png)

Scheme 45. Synthesis of transition metal carbonyl complexes of carbene-phosphinidene adducts 6·PH, 6·PPh and 6·PMes.

![Scheme 46](image.png)

Scheme 46. Synthesis of tungsten(0) carbonyl complexes of 5·PH.

The reactivity of carbene-phosphinidene adduct 6·PH towards group 8 and 9 metal complexes has been investigated by Tamm and co-workers (Scheme 47). Addition of dimeric complexes of the type [LMCl₂]₂ (M = Ru, Os, Rh, Ir) to 6·PH afforded the three-legged piano-stool complexes [(6·PH)M(L)Cl₂] 72 (M = Ru/Os, L
= \eta^6\text{-}p\text{-}cymene) and 73 (M = Rh/Ir, L = \eta^5\text{-}C_5Me_5), which upon dehydrochlorination with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) can partly be converted into the corresponding NHC-phosphinidenyl complexes 76 and 77 (see 1.4.4 and Scheme 49).[51]

\[ \text{Scheme 47. Reactions of carbene-phosphinidene adduct 6\text{-}PH with ruthenium(II), osmium(II), rhodium(III) and iridium(III) complexes.} \]

Slootweg, Grützmacher and co-workers explored the reactivity of carbene-phosphinidene adduct 1\text{-}PPh towards ZnCl_2 (Scheme 48). Namely, reaction of 1\text{-}PPh with half an equivalent of ZnCl_2 led to bis(1\text{-}PPh) zinc complex 74, which upon addition of another half equivalent of ZnCl_2 afforded the 1:1 zinc carbene-phosphinidene complex 75.[9] The latter can also be obtained directly by treating 1\text{-}PPh with one equivalent of ZnCl_2. Interestingly, ZnCl_2 complexation of NHC-phosphinidene adduct 1\text{-}PPh induced selective phenylphosphinidene transfer reactions to electron-poor heterodienes (see 1.4.5 and Scheme 53).
Scheme 48. Synthesis of ZnCl₂ complexes of carbene-phosphinidene adduct 1·PPh.

1.4.4. Substitution reactions with transition-metal complexes

Besides complexation, NHC=PH and NHC=Psilyl adducts can undergo substitution reactions with transition-metal halides. Tamm and co-workers reacted 6·PSiMe₃ with the dinuclear metal halides [LMCl₂]₂ (M = Ru/Os, L = η⁶-p-cymene; M = Rh/Ir, L = η⁵-C₅Me₅) and [Rh(cod)Cl]₂ to afford, after elimination of trimethylsilyl chloride, the NHC-phosphinidenyl metal complexes 76–78 that display two-legged piano stool geometries in the solid state where the anionic 6·P ligand acts as a strong 2σ,2π-electron donor (Scheme 49). Complexes 76–78 can be reacted further with AuCl(SMe₂) to yield bimetallic complexes 76·AuCl, 77·AuCl and trimetallic complex 78·AuCl (see Scheme 49) with three- and four-coordinated phosphorus atoms, respectively.
Grützmacher, Pringle and co-workers have demonstrated that the parent NHC=PHs 6-PH and 11-PH can be converted into the corresponding linear bis(carbene-phosphinidenyl) Hg complexes 79 and 80 by treatment with half an equivalent of mercury(II) chloride in the presence of DBU (Scheme 50). \[29\]

**Scheme 49.** Synthesis of carbene-phosphinidenyl complexes of ruthenium(II), osmium(II), rhodium(III), iridium(III) and rhodium(I).

**Scheme 50.** Synthesis of mercury(II) phosphinidenyl complexes. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.
1.4.5. Phosphinidene transfer reactions

The first example of transfer of a phosphorus moiety from the NHC-stabilized molecules described in this review was reported by Grützmacher and co-workers. Namely, $P_3$ radical 38 (Scheme 35) undergoes cycloaddition with dimethyl acetylenedicarboxylate with concomitant elimination of the two NHC fragments, followed by electron transfer to give the ion pair 82 (Scheme 51). This $P_3$ transfer reaction indicates that NHCs can stabilize reactive phosphorus fragments, but also facilitate their subsequent transfer to substrate molecules, which stimulated the quest for facile phosphinidene transfer reactions from NHC=PR adducts.

![Scheme 51. P$_3$ transfer reaction from 38 to an activated alkyne to give 82.](image)

Weber and co-workers demonstrated that the acyclic carbene–phosphinidene adducts (Me$_2$N)$_2$C=PR (R = iBu, Cy, 1-Ad, Ph, Mes) can transfer the [PR] moiety to diphenylketene.$^{[53]}$ Slootweg, Grützmacher and co-workers developed a related protocol for the sterically unencumbered N-heterocyclic carbene phosphinidene adduct 1·PPh that acts as a phenylphosphinidene transfer agent in the presence of organic electrophiles (Scheme 52). Treatment of 1·PPh with 9,10-phenanthrenequinone resulted in formation of dioxyphosphine oxide 83 and quinone-methide 84, while addition of trans-chalcone led to an intractable mixture of products, from which oxo-3-phospholene 85 and the zwitterionic carbene-chalcone adduct 86 could be isolated. Diphenylketene also proved in this case to
be a suitable substrate for phosphinidene transfer. Its reaction with 1-PPh resulted in the formation of 1,3-oxaphospholan-5-one 87 as the sole phosphorus-containing product, while an additional equivalent of ketene was consumed to trap the liberated carbene 1 to afford adduct 88 (Scheme 52).[9]

![Scheme 52. Reactivity of 1-PPh towards ortho-quinone, trans-chalcone and diphenylketene.](image_url)

Arduengo and co-workers discovered that the Lewis acid BPh$_3$ is capable of liberating phenylphosphinidene from 5-PPh, which was derived from the detection of the cyclopolyphosphines (PPh)$_3$, (PPh)$_4$ and (PPh)$_5$ in the reaction mixture (Scheme 27).[44] Similarly, Slootweg, Grützmacher et al. showed that treatment of 1-PPh with BPh$_3$, AlCl$_3$, MgCl$_2$ or Zn(OAc)$_2$ leads to phenylphosphinidene extrusion and the formation of the oligomeric phosphinidenes (PPh)$_n$ ($n = 3-5$).[9] Selective transfer of the extruded phosphinidene to suitable substrates is possible when ZnCl$_2$ is used as Lewis acid. Thus, zinc complex 75 allowed phenylphosphinidene transfer to form phosphonite 89 in the reaction with 9,10-phenanthrenequinone, oxo-3-phospholene 85 when applying trans-chalcone, and a mixture of 1,4,2-dioxaphospholane 91 and 1,3-oxaphospholan-5-one 87 while using diphenylketene.
as substrate. In all cases, ZnCl$_2$ captured the liberated carbene to form the insoluble one-dimensional coordination polymer [1·ZnCl$_2$]$_n$ (Scheme 53).  

**Scheme 53.** Reactivity of zinc complex 75 towards phenanthrene-9,10-quinone, trans-chalcone and diphenylketene.

### 1.5. Summary and Conclusion

The past five years have shown the emergence and remarkable development of the chemistry of N-heterocyclic carbene-phosphinidene adducts. A plethora of P substituents and stabilizing carbenes have been applied via a multitude of synthetic pathways to create these electron rich NHC=PR adducts that display many addition reactions with organic, main-group as well as transition-metal based electrophiles. In addition, the P–H, P–Cl, and P–SiMe$_3$ substituted analogues display facile substitution reactions expanding the scope of differently substituted N-heterocyclic carbene-phosphinidene adducts dramatically. With an increasing emphasis on applicability, the NHC=PR adducts have already been applied as ligands in homogeneous transition-metal based catalysis and as phosphinidene transfer
agents providing access to organophosphorus compounds that are difficult to obtain otherwise. Intuitively, much more can be expected from this field, which will lead to exciting discoveries in the coming years.

### 1.6 References


N-heterocyclic Carbene-Phosphiniden Adducts: Synthesis, Properties and Applications


