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### Advances in organophosphorus chemistry

*Synthesis, reactivity and recycling*

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# Chapter 1

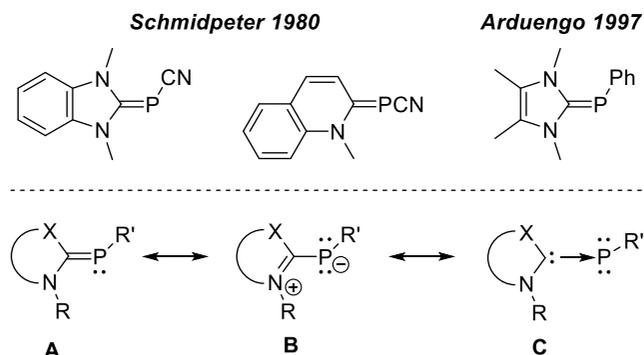
## *N-heterocyclic Carbene-Phosphinidene Adducts: Synthesis, Properties and Applications*

**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 phosphalkenes.

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## 1.1 Introduction

The combination of a low-valent N-heterocyclic carbene<sup>[1]</sup> and a transient phosphinidene<sup>[2]</sup> creates an electron-rich phosphalkene that was highlighted for the first time by Arduengo and co-workers in 1997<sup>[3]</sup> and early examples were reported by Schmidpeter in 1980 (Scheme 1).<sup>[4]</sup> 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),<sup>[ 5 ]</sup> particularly bis(amino)carbenes and (alkyl)(amino)carbenes (CAACs).<sup>[6]</sup>



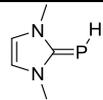
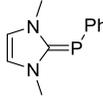
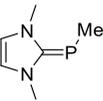
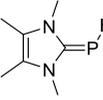
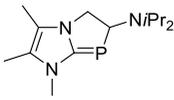
**Scheme 1.** The first reported examples by Schmidpeter and Arduengo *et al.* (top) and canonical forms of NHC-phosphinidene adducts, X = CR<sub>2</sub>, NR or S (bottom).

Carbene-phosphinidene adducts (NHC=PR) can be regarded as inversely polarized phosphalkenes<sup>[7]</sup> 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

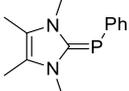
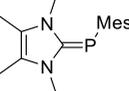
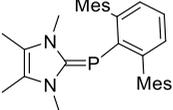
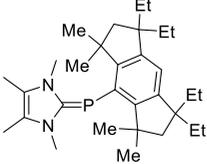
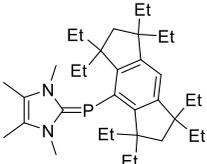
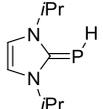
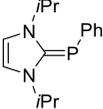
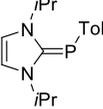
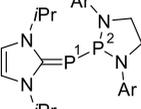
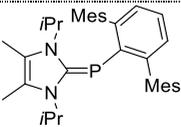
of a given NHC=PR adduct depends on the phosphorus substituent and the nature of the carbene.

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 imidazolylienes (**1-9**), followed by those of imidazolinylienes (**10, 11**), amido carbenes (**12-14**), tetrahydropyrimidinylidenes (**15, 16**), thiazolyliene (**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.**  $^{31}\text{P}$ ,  $^{13}\text{C}$  NMR chemical shifts ( $\text{P}=\text{C}_{\text{NHC}}$ ) (recorded in  $\text{C}_6\text{D}_6$  unless stated otherwise) and selected structural data for the adducts **1-PR-22-PR**.

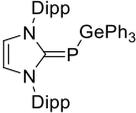
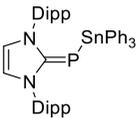
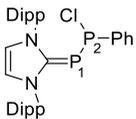
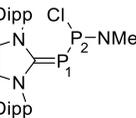
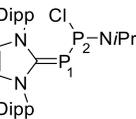
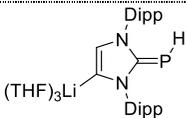
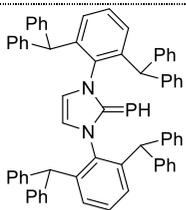
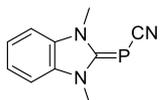
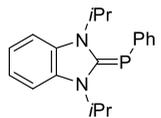
Compound	Name <sup>[Ref]</sup>	$\delta^{31}\text{P}$ , ppm	$\delta^{13}\text{C}$ , ppm	$\text{C}_{\text{NHC}}=\text{P}$ bond, Å	C-P-R angle, °	Torsion angle N-C-P-R, °
	<b>1-PH</b> <sup>[8]</sup>	-149.3	176.0	1.763(3)	96.0(15)	0.9(18)
	<b>1-PPh</b> <sup>[9]</sup>	-49.1	170.1	1.7917(14) [1.7911(15)] <sup>[a]</sup>	101.30(6) [99.98(7)] <sup>[a]</sup>	48.01(16) [50.42(15)] <sup>[a]</sup>
	<b>1-PMes</b> <sup>[10]</sup>	-73.8	169.9	1.768(4)	104.6(2)	32.5(4)
	<b>2-PH</b> <sup>[8]</sup>	-148.8	174.7 <sup>[b]</sup>	1.7721(14) [1.7739(18)] <sup>[a]</sup>	95.9(8) [96.2(15)] <sup>[a]</sup>	0.2(8) [1.6(16)] <sup>[a]</sup>
	<b>(2-H)</b> PCHN(iPr) <sub>2</sub> <sup>[11]</sup>	-64.8 <sup>[c]</sup>	178.9 <sup>[c]</sup>	-	-	-

Chapter 1

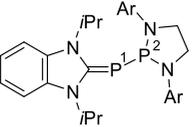
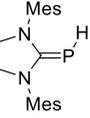
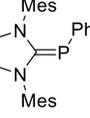
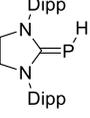
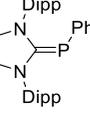
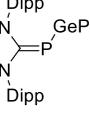
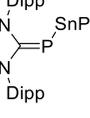
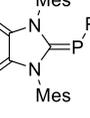
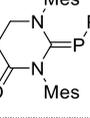
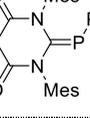
	2·PPh <sup>[3]</sup>	-53.5 <sup>[b]</sup>	169.1 <sup>[b]</sup>	1.794(3)	102.34(14)	51.0(3)
	2·PMes <sup>[12]</sup>	-75.1	-	-	-	-
	2·P(Dmp) <sup>[13]</sup>	-76.7	-	1.786(4)	99.10(17)	55.5(4)
	2·P(EMind) <sup>[14]</sup>	-70.5	168.3	-	-	-
	2·P(Eind) <sup>[14]</sup>	-63.9	168.6	1.767(3)	102.72(12)	3.4(3)
<hr/>						
	3·PH <sup>[8]</sup>	-149.9 <sup>[b]</sup>	173.7 <sup>[b]</sup>	-	-	-
	3·PPh <sup>[15,16]</sup>	-61.2 <sup>[15]</sup> -60.0 <sup>[16]</sup>	167.8 <sup>[15]</sup> 168.2 <sup>[16]</sup>	-	-	-
	3·P(pTol) <sup>[16]</sup>	-57.0 <sup>[c]</sup>	-	-	-	-
	3·P(DAP) <sup>[17]</sup>	-68.2 P <sup>1</sup> (177.3 P <sup>2</sup> )	166.8	-	-	-
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	4·P(Dmp) <sup>[13]</sup>	-75.0	171.3	1.799(3)	101.53(11)	57.1(2)

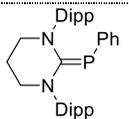
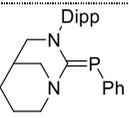
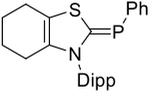
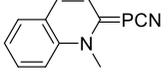
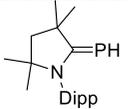
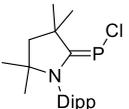
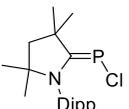
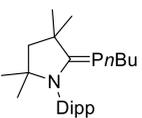
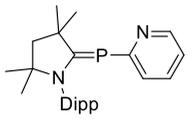
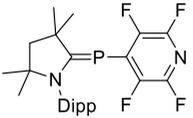
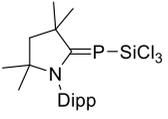
	<b>5·PH</b> <sup>[18,8]</sup>	-147 <sup>[18]</sup> -147.3 <sup>[8]</sup>	- 180.0 <sup>[b]</sup>	1.747(3) 1.747(2)	100(2) 101(2)	5(2) 3(2)
	<b>5·PCF<sub>3</sub></b> <sup>[19]</sup>	-23.6	168.1	1.784(2)	101.66(8)	31.3(2)
	<b>5·PPh</b> <sup>[19]</sup>	-23.0	170.0 <sup>[b]</sup>	1.763(6)	99.9(3)	26.5(7)
	<b>5·PMes</b> <sup>[12]</sup>	-59.1	-	1.769(3)	104.90(11)	8.3(3)
	<b>5·PGePh<sub>3</sub></b> <sup>[20]</sup>	-155.2 <sup>[d]</sup>	168.7 <sup>[d]</sup>	-	-	-
	<b>5·PSnPh<sub>3</sub></b> <sup>[20]</sup>	-179.5 <sup>[d]</sup>	169.4 <sup>[d]</sup>	1.778(3)	111.51(9)	7.1(3)
	<b>6·PH</b> <sup>[21,22,23]</sup>	-134.3 <sup>[21]</sup> -136.7 <sup>[22]</sup> -133.8 <sup>[23]</sup>	180.5 <sup>[21]</sup> 180.2 <sup>[22]</sup> 180.9 <sup>[23]</sup>	- 1.752(1) <sup>[22]</sup> 1.7509(15) <sup>[23]</sup>	- 94.5(7) 94.9(12)	- 1.2(6) 1.4(10)
	<b>6·PPh</b> <sup>[15,24]</sup>	-18.9 <sup>[15]</sup> -19.4 <sup>[24]</sup>	172.9 <sup>[15]</sup> -	- 1.7658(10) <sup>[24]</sup>	- 104.61(4)	- 24.5
	<b>6·PMes</b> <sup>[12]</sup>	-52.1	-	1.766(2)	105.74(11)	13.8(2)
	<b>6·PSiMe<sub>3</sub></b> <sup>[23]</sup>	-129.5	175.2	1.7744(13)	110.71(4)	41.01(14)

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	<b>6-PGePh<sub>3</sub></b> <sup>[20]</sup>	-145.1	174.4	1.7748(16)	110.07(5)	46.89(16)
	<b>6-PSnPh<sub>3</sub></b> <sup>[20]</sup>	-161.5	174.8	1.774(3)	110.99(9)	26.2(3)
	<b>6-PPClPh</b> <sup>[25]</sup>	-17.3 P <sup>1</sup> (157.6 P <sup>2</sup> ) <sup>[b]</sup>	169.9 <sup>[b]</sup>	1.8017(18)	96.35(6)	44.18(18)
	<b>6-PPClNMe<sub>2</sub></b> <sup>[25]</sup>	-33.5 P <sup>1</sup> (214.1 P <sup>2</sup> ) <sup>[b]</sup>	170.7 <sup>[b]</sup>	-	-	-
	<b>6-PPClNPr<sub>2</sub></b> <sup>[25]</sup>	-18.4 P <sup>1</sup> (215.1 P <sup>2</sup> ) <sup>[b]</sup>	171.6	1.7835(16)	97.14(5)	36.63(19)
	<b>Li-6-PH</b> <sup>[26]</sup>	-143.0	-	1.763(2)	102	0
	<b>7-PH</b> <sup>[27]</sup>	-134.5 <sup>[e]</sup>	177.3 <sup>[e]</sup>	1.755(4)	97(2)	3(3)
	<b>8-PCN</b> <sup>[4]</sup>	-133	-	1.771(5)	101.8(5)	-
	<b>9-PPh</b> <sup>[15]</sup>	-34.6	177.4	-	-	-

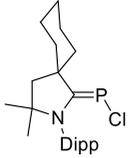
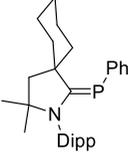
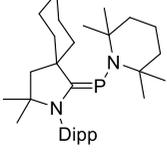
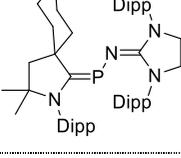
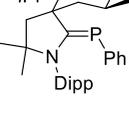
*N*-heterocyclic Carbene-Phosphenidene Adducts: Synthesis, Properties and Applications

	<b>9-P(DAP)<sup>[177]</sup></b>	-35.5 P <sup>1</sup> (166.3 P <sup>2</sup> )	177.1	-	-	-
	<b>10-PH<sup>[28]</sup></b>	-127.2	191.0 <sup>[b]</sup>	1.7464(16)	99.3(14)	3.4(14)
	<b>10-PPh<sup>[19]</sup></b>	-12.0 <sup>[b]</sup> -10.4	184.3 <sup>[b]</sup>	1.746(4)	100.5(2)	19.5(5)
	<b>11-PH<sup>[29]</sup></b>	-116.7 <sup>[b]</sup>	195.1	1.743(2)	104.2(17)	1.8(16)
	<b>11-PPh<sup>[15]</sup></b>	-10.2 <sup>[e]</sup>	186.9 <sup>[e]</sup>	-	-	-
	<b>11-PGePh<sub>3</sub><sup>[20]</sup></b>	-114.7 <sup>[d]</sup>	192.5 <sup>[d]</sup>	-	-	-
	<b>11-PSnPh<sub>3</sub><sup>[20]</sup></b>	-124.6	193.1	-	-	-
	<b>12-PPh<sup>[30]</sup></b>	78.6	169.9	1.691(4)	106.65(17)	0.77
	<b>13-PPh<sup>[15,30]</sup></b>	39.7 <sup>[15]</sup> 37.7 <sup>[30]</sup>	180.3 <sup>[15]</sup> 180.1 <sup>[e]</sup>	-	-	-
	<b>14-PPh<sup>[30]</sup></b>	83.0	172.0 <sup>[e]</sup>	1.726(3)	108.22(13)	9.83

	<b>15·PPh</b> <sup>[15]</sup>	14.8	186.5	-	-	-
	<b>16·PPh</b> <sup>[15]</sup>	34.9	199.9	-	-	-
	<b>17·PPh</b> <sup>[15]</sup>	57.0	192.0	-	-	-
	<b>18·PCN</b> <sup>[4]</sup>	-38	-	-	-	-
	<b>(E/Z)19·PH</b> <sup>[31]</sup>	-38.3 -44.9	212.3 217.2	-	-	-
	<b>E-19·PCl</b> (94.5 %) <sup>[31]</sup>	161.9	210.9	1.7354(11)	103.64(4)	179.74(7)
	<b>Z-19·PCl</b> (5.5 %) <sup>[31]</sup>	129.4	-	1.686(6) <sup>[f]</sup>	96.3(3)	19.7(7)
	<b>19·PnBu</b> <sup>[32]</sup>	61.2	206.3	-	-	-
	<b>19·P(o-Py)</b> <sup>[32]</sup>	65.4	209.5	-	-	-
	<b>19·P(p-C<sub>5</sub>F<sub>4</sub>N)</b> <sup>[32]</sup>	-4.3	208.2	-	-	-
	<b>19·PSiCl<sub>3</sub></b> <sup>[32]</sup>	-22.0 <sup>[b]</sup>	217.4 <sup>[b]</sup>	-	-	-

*N*-heterocyclic Carbene-Phosphenidene Adducts: Synthesis, Properties and Applications

	<b>19-P(SiCl<sub>2</sub>L)</b> [33]	59.0	213.4	1.732(2)	116.43(7)	169.36(12)
	<b>19-P(SiL)</b> <sup>[33]</sup>	68.8	216.8	1.7303(17) [1.7381(18)] <sup>a</sup>	108.93(6) [107.05(6)] <sup>[a]</sup>	177.96(12) 175.83(11)] <sup>[a]</sup>
	<b>19-PGeCl<sub>3</sub></b> [32]	47.8 <sup>[b]</sup>	219.6	1.7653(12)	107.74(4)	161.66(8)
	<b>19-PPCl<sub>2</sub></b> <sup>[32]</sup>	73.9 (242.5) <sup>[b]</sup>	215.3	-	-	-
	<b>19-PPCl(Cy)</b> [32]	53.5 (135.8)	217.4	-	-	-
	<b>19-PPPh<sub>2</sub></b> <sup>[32]</sup>	41.2 (-27.3)	214.3	-	-	-
<hr/>						
	<b>E-20-PCI</b> (96.3 %) <sup>[31]</sup>	160.3	208.2	1.7404(12)	104.05(4)	178.52(7)
	<b>Z-20-PCI</b> (3.7 %) <sup>[31]</sup>	131.1	-	1.434(12) <sup>[f]</sup>	98.3(7)	4.7(12)
	<b>20-P(DAP)</b> [17]	76.3 P <sup>1</sup> (156.6 P <sup>2</sup> )	219.4	-	-	-
<hr/>						
	<b>E-21-PCI</b> (86.3 %) <sup>[31]</sup>	163.4	210.1	1.7513(15)	104.51(5)	178.68(10)

	<b>Z-21·PCI</b> (13.7 %) <sup>[31]</sup>	135.0	-	1.615(4) <sup>[f]</sup>	98.0(2)	6.8(5)
	<b>21·PPh<sup>[15]</sup></b>	68.9	208.1	1.7336(15)	104.94(6)	179.02(11)
	<b>21·P(TMP)</b> <sup>[34]</sup>	135.4	207.3	1.7376(14)	108.90(6)	177.00
	<b>21·PN=SIPr</b> <sup>[35]</sup>	134.0	199.2	1.719(2)	102.78(9)	177.30(15)
	<b>22·PPh<sup>[15]</sup></b>	56.2	191.3	1.743(8)	116.6(4)	13.3(10)
				[1.738(8), 1.737(8), 1.723(8)] <sup>[a]</sup>	[115.2(4), 116.0(4), 115.7(4)] <sup>[a]</sup>	[4.2(9), 8.0(11), 4.0(10)] <sup>[a]</sup>

[a] Values for the other independent molecules are shown in square brackets. [b] The NMR spectrum was recorded in THF-*d*<sub>6</sub>. [c] The NMR spectrum was recorded in Toluene-*d*<sub>6</sub>. [d] The NMR spectrum was recorded in CD<sub>2</sub>Cl<sub>2</sub>. [e] The NMR spectrum was recorded in CDCl<sub>3</sub>. [f] Due to the low occupancy all values for the minor isomer have a high estimated standard deviation. Mes = 2,4,6-trimethylphenyl, Dmp = 2,6-dimesitylphenyl, *p*Tol = *p*-tolyl, Cy = cyclohexyl, DAP = 1,3-bis-Ar-1,3,2-diazaphospholidine, Ar = 2,6-bis[(4-*tert*-butylphenyl)methyl]-4-methylphenyl (see also Scheme 18), Dipp = 2,6-diisopropylphenyl, L = benzamidine, TMP = 2,2,6,6-tetramethylpiperidine, SIPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene.

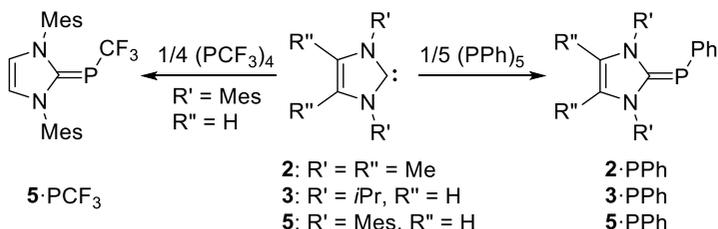
## 1.2. Synthesis of N-heterocyclic Carbene-Phosphinidene Adducts

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)<sub>5</sub> at room temperature to afford **2**·PPh ( $\delta^{31}\text{P} = -53.5$ ) in 79% isolated yield (Scheme 2).<sup>[3]</sup> The upfield <sup>31</sup>P NMR spectroscopy chemical shift proved to be characteristic for inversely polarized phosphalkenes.<sup>[5a]</sup> 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)° between the imidazole ring and the P–C<sub>Ph</sub> bond, which indicates a weak P<sub>π</sub>–C<sub>π</sub> 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;  $\delta^{31}\text{P} = -23.0$ ) and (trifluoromethyl)phosphinidene (**5**·PCF<sub>3</sub>;  $\delta^{31}\text{P} = -23.6$ ) in 67 and 90% yield, respectively (Scheme 2).<sup>[19]</sup>

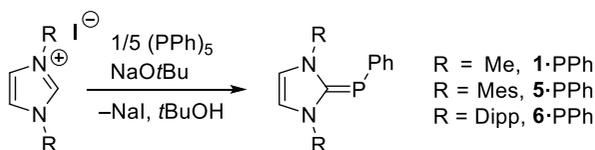


**Scheme 2.** Synthesis of carbene-phosphinidene adducts from carbenes and cyclopolyphosphines.

The larger N-substituent of **5** (versus **2**) causes a downfield shift of the <sup>31</sup>P NMR signal of **5**·PPh, and in the solid state a reduced N–C–P–R dihedral angle of 26.5(7)°, allowing  $\pi$ – $\pi$  stacking of the P–Ph and N–Mes rings. The related **5**·PCF<sub>3</sub> displays similar values (P–C<sub>NHC</sub> 1.784(2) Å, N–C–P–R 31.3(2)°; see Table 1).<sup>[19]</sup> In

2013, Bertrand and co-workers showed that 1,3-di-*iso*-propylimidazol-2-ylidene (**3**) can also be used and synthesized **3**·PPh (79%,  $\delta^{31}\text{P} = -61.2$ ; Scheme 2) in a similar fashion.<sup>[15]</sup>

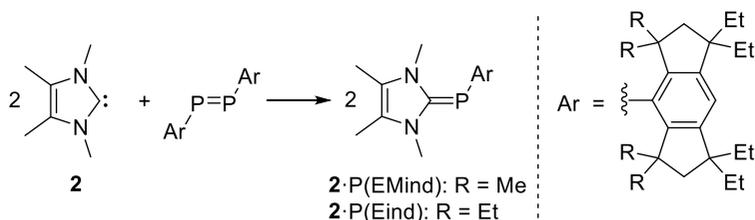
The groups of Slootweg and Grützmacher have extended this synthetic methodology by showing that carbenes can also be generated *in situ*, and synthesized **1**·PPh, **5**·PPh and **6**·PPh from the corresponding imidazolium salts, (PPh)<sub>5</sub> and sodium *tert*-butoxide in an efficient one-pot synthesis in high yields (87–95%; Scheme 3).<sup>[9]</sup> **1**·PPh ( $\delta^{31}\text{P} = -49.1$ ; P–C<sub>NHC</sub> 1.7917(14) Å, N–C–P–R 48.01(16)°; 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)<sub>5</sub> and NaOtBu.

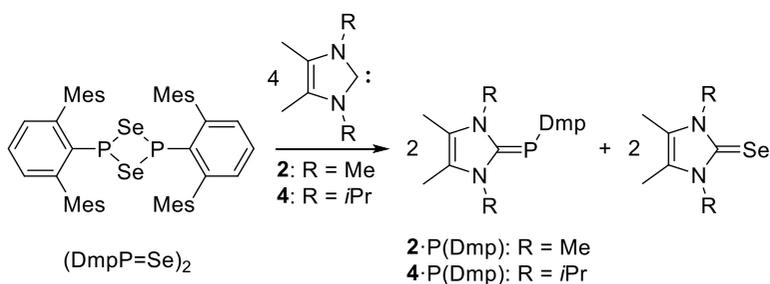
### 1.2.2. Diphosphenes

In analogy to the use of cyclopolyposphines (RP)<sub>n</sub>, 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-ylidene (**2**), which resulted in the quantitative formation of the NHC-phosphinidene adducts **2**·P(EMind) ( $\delta^{31}\text{P} = -70.5$ ) and **2**·P(Eind) ( $\delta^{31}\text{P} = -63.9$ ; Scheme 4).<sup>[14]</sup> 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–C bond of 1.767(3) Å and a N–C–P–R dihedral angle of 3.4(3)°.



**Scheme 4.** Synthesis of carbene-phosphinidene adducts using diphosphenes as phosphorus sources.

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

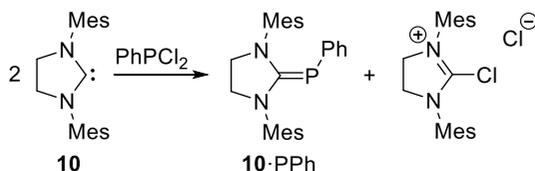


**Scheme 5.** Synthesis of carbene-phosphinidene adducts using the phosphinidene selenide dimer  $(\text{DmpP}=\text{Se})_2$ .  $\text{Dmp} = 2,6\text{-dimesitylphenyl}$ .

### 1.2.3. Chlorophosphines

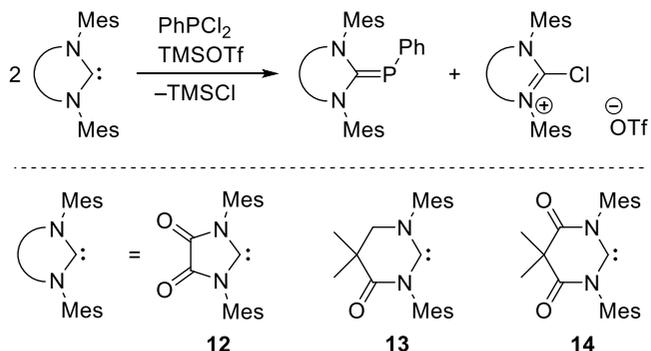
$\text{NHC}=\text{PR}$  adducts can also be prepared from carbenes and dichlorophosphines. Arduengo *et al.* showed that 2 equivalents of 1,3-dimesitylimidazol-2-ylidene (**10**) react with dichlorophenylphosphine to afford

**10**·PPh ( $\delta^{31}\text{P} = -10.4$ ) in 69% isolated yield after removal of the 2-chloro-1,3-dimesitylimidazolium chloride byproduct by filtration (Scheme 6).<sup>[19]</sup> 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<sub>NHC</sub> 1.763(6) Å, N–C–P–R 26.5(7)°; **10**·PPh: P–C<sub>NHC</sub> 1.746(4) Å, N–C–P–R 19.5(5)°; see Table 1, section 3.3 and Scheme 26).



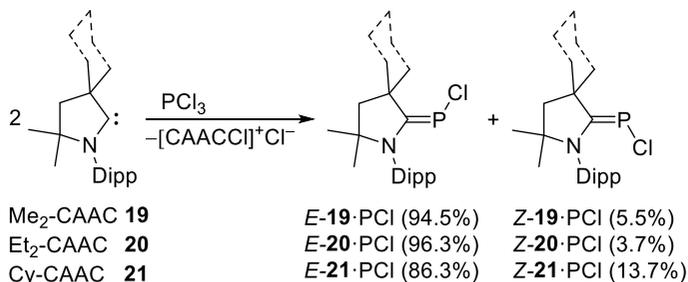
**Scheme 6.** Preparation of carbene-phosphinidene adduct **10**·Ph by carbene addition to phenyldichlorophosphine.

Hudnall *et al.* modified Arduengo's protocol to accommodate  $\pi$ -accepting carbonyl-decorated carbenes. They showed that treatment of PhPCl<sub>2</sub> with two equivalents of the carbenes **12**–**14** in the presence of trimethylsilyl triflate (1.0 equiv) afforded the adducts **12**·PPh ( $\delta^{31}\text{P} = 78.6$ ; P–C<sub>NHC</sub> 1.691(4) Å, N–C–P–R 0.77°), **13**·PPh ( $\delta^{31}\text{P} = 37.7$ ) and **14**·PPh ( $\delta^{31}\text{P} = 83.0$ ; P–C<sub>NHC</sub> 1.726(3) Å, N–C–P–R 9.83°) along with their 2-chloro-iminium triflate salts in modest yields (31.9–55.4%) (Scheme 7).<sup>[30]</sup> 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  $\text{PhPCl}_2$  in the presence of trimethylsilyl triflate (TMSOTf).

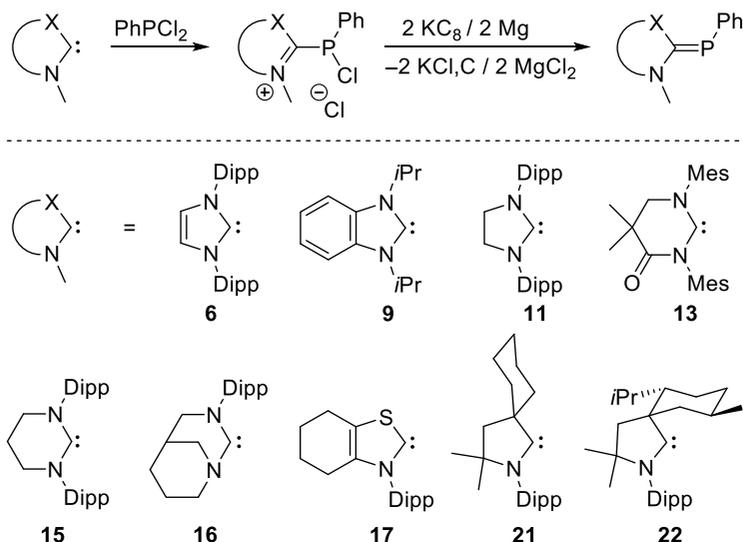
The generation of carbene-phosphinidene adducts can also be achieved using phosphorus trichloride. Roesky and co-workers reported the addition of  $\text{PCl}_3$  to three different cyclic (alkyl)(amino)carbenes (CAACs; 2 equiv), which resulted in the formation of chlorophosphinidene adducts **19–21**· $\text{PCl}$  as mixtures of *E*- and *Z*-isomers concomitant with the formation of  $[\text{CAACCl}]^+\text{Cl}^-$  as by-product (Scheme 8).<sup>[31]</sup>



**Scheme 8.** Synthesis of CAAC-chlorophosphinidene adducts.

Bertrand and co-workers reported a general two-step procedure for making  $\text{NHC}=\text{PR}$  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,

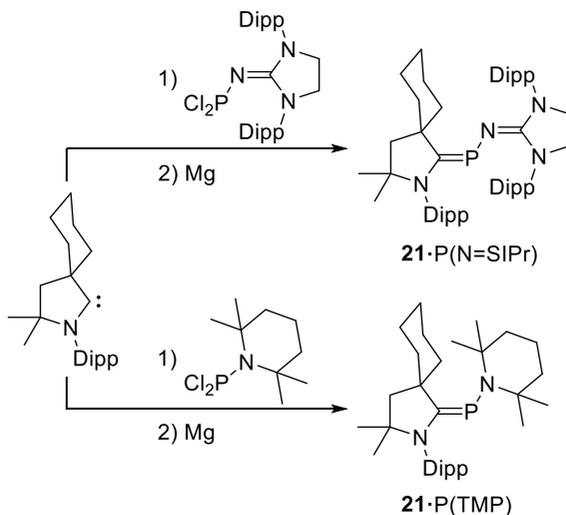
after reduction ( $\text{KC}_8$  or Mg) and subsequent work-up, afford the carbene-phosphinidene adducts (**6**, **9**, **11**, **13**, **15–17**, **21**, **22**)-PPh in 10–85% yield (Scheme 9; Table 1).<sup>[15]</sup>



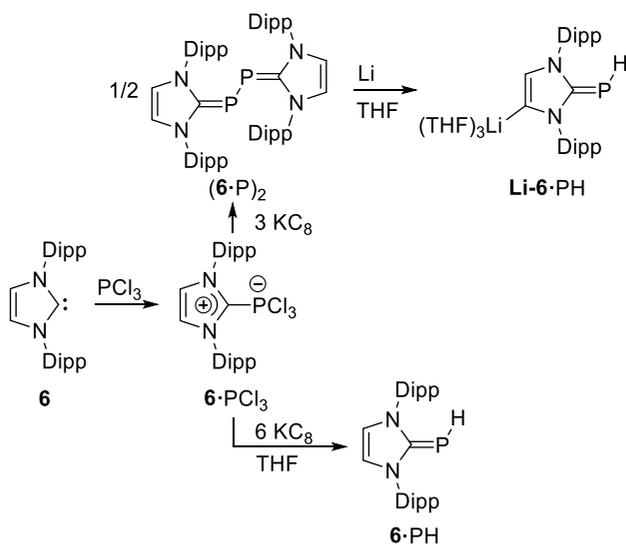
**Scheme 9.** Bertrand's two-step synthesis of  $\text{NHC}=\text{PR}$  adducts from carbenes and  $\text{PhPCl}_2$  followed by reduction.

In a similar fashion cyclic (alkyl)(amino)carbene-phosphinidene adducts **21**·P(N=SiPr) ( $\delta^{31}\text{P} = 134.0$ )<sup>[35]</sup> and **21**·P(TMP) ( $\delta^{31}\text{P} = 135.4$ )<sup>[34]</sup> 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  $\text{PCl}_3$  with N-heterocyclic carbene **6** leads to adduct **6**· $\text{PCl}_3$ , which upon reduction with three equivalents of potassium graphite yields carbene-stabilized diphosphorus (**6**·P)<sub>2</sub> (56.6%;  $\delta^{31}\text{P} = -52.4$ )<sup>[36]</sup> and further reduction with Li metal afforded the anionic NHC–parent phosphinidene adduct **Li**·**6**·PH (16.3%;  $\delta^{31}\text{P} = -143.0$ ; Scheme 11).<sup>[26]</sup> However, reduction of **6**· $\text{PCl}_3$  with six equivalents of potassium graphite afforded the neutral **6**·PH in 20% isolated yield ( $\delta^{31}\text{P} = -133.9$ ; Scheme 11), as reported by Tamm *et al.*<sup>[23]</sup>



**Scheme 10.** Bertrand's two-step synthesis of phosphinidene adducts of CAAC.

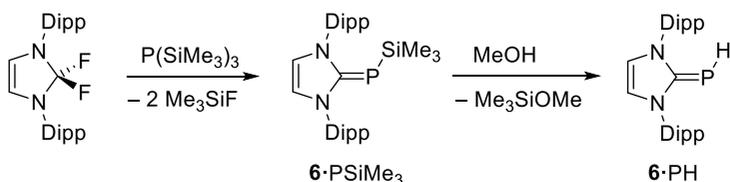


**Scheme 11.** Synthesis of carbene-phosphinidene adducts using  $\text{PCl}_3$ .

#### 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-

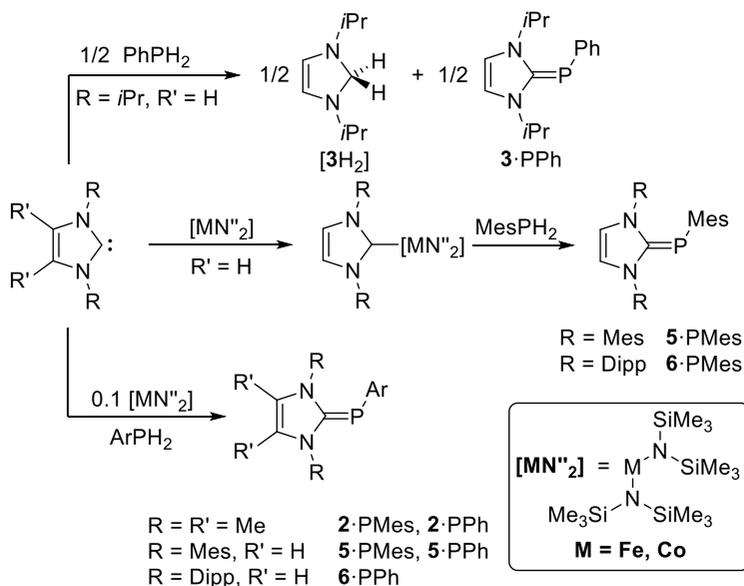
diisopropylphenyl)-2,2-difluoroimidazoline (“PhenoFluor”) with  $\text{P}(\text{SiMe}_3)_3$  gives silylphosphinidene adduct  $\mathbf{6}\cdot\text{PSiMe}_3$  ( $\delta^{31}\text{P} = -129.5$ ) in 83% isolated yield, which upon methanolysis converts readily to the parent phosphinidene adduct  $\mathbf{6}\cdot\text{PH}$  ( $\delta^{31}\text{P} = -133.8$ ) in 81% yield (Scheme 12). Subsequently,  $\mathbf{6}\cdot\text{PSiMe}_3$  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).<sup>[23]</sup>



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

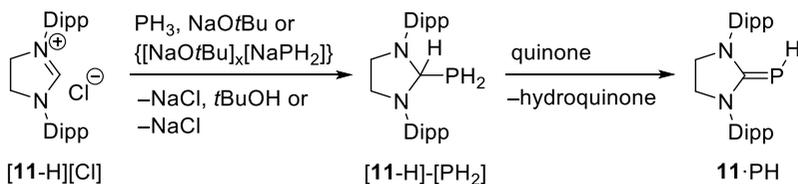
Primary phosphines follow a similar reaction course as the corresponding dichlorophosphines. Radius and co-workers showed that the reaction of one equivalent of phenylphosphine with two equivalents of 1,3-di-*iso*-propylimidazol-2-ylidene (**3**) leads to carbene-phosphinidene adduct  $\mathbf{3}\cdot\text{PPh}$  ( $\delta^{31}\text{P} = -60.0$ ) after 5 h at 105 °C in a quantitative yield next to the  $[\mathbf{3H}_2]$  by-product (Scheme 13).<sup>[16]</sup> When equimolar amounts of carbene and phosphine were used, also the cyclopolyphosphines  $(\text{PPh})_4$ ,  $(\text{PPh})_5$  and  $(\text{PPh})_6$  were detected by  $^{31}\text{P}$  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  $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2]$  ( $\text{M} = \text{Fe}, \text{Co}$ ), N-heterocyclic carbenes **2**, **5** and **6** react with phenyl or mesitylphosphines at 80 °C to give the carbene-phosphinidene adducts  $(\mathbf{2},\mathbf{5},\mathbf{6})\cdot\text{PPh}$  and  $(\mathbf{2},\mathbf{5},\mathbf{6})\cdot\text{PMes}$  (Scheme 13).<sup>[12]</sup> The formation of  $\mathbf{2}\cdot\text{PMes}$  is also catalyzed by the phosphinidene-bridged complex  $[(\mathbf{2})_2\text{Fe}(\mu\text{-PMes})]_2$ , which provides evidence for metal-catalyzed phosphinidene transfer.



**Scheme 13.** Access to carbene-phosphinidene adducts from primary phosphines.

Phosphine gas ( $\text{PH}_3$ ) 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)imidazol-2-ylidene (**11**) inserts into the P–H bond of  $\text{PH}_3$ , giving access to phosphinyl–imidazolidine [**11-H**]- $[\text{PH}_2]$ , which upon dehydrogenation by 9,10-phenanthrenequinone yields the parent phosphinidene–carbene adduct **11**·PH ( $\delta^{31}\text{P} = -116.7$ ; Scheme 14).<sup>[29]</sup>

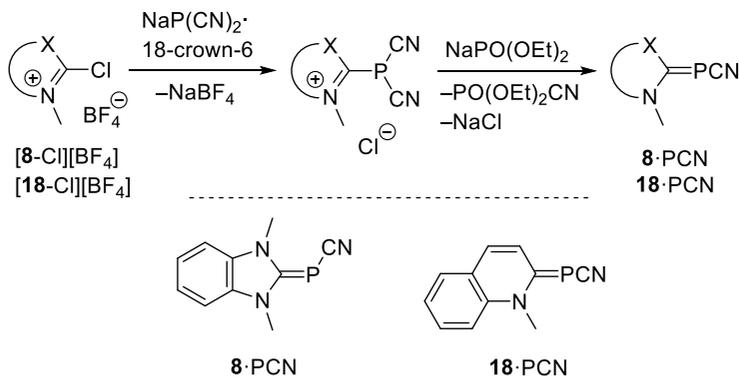


**Scheme 14.** Synthesis of carbene-phosphinidene adduct **11**·PH from imidazolium salt and  $\text{PH}_3$  or  $\{[\text{NaOtBu}]_x[\text{NaPH}_2]\}$  ( $x \approx 2.5$ ). Quinone = 9,10-phenanthrenequinone.

## 1.2.5. Phosphides

Alternatively, **11**·PH can be synthesized via the reaction between sodium *tert*-butoxide/sodium dihydrogenphosphide aggregate  $\{[\text{Na}(\text{O}t\text{Bu})]_x[\text{Na}(\text{PH}_2)]\}$  ( $x \approx 2.5$ ) and imidazolium chloride [**11**-H][Cl] followed by dehydrogenation (Scheme 14).<sup>[29]</sup>

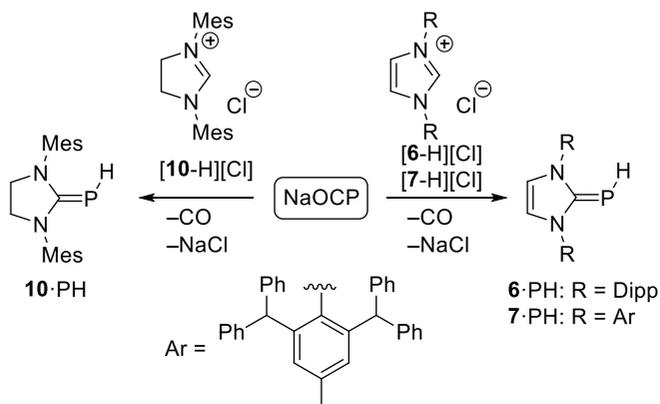
Interestingly, the first reported synthesis of N-heterocyclic carbene-phosphinidene adducts was also achieved using phosphides. In 1980, Schmidpeter and co-workers showed that carbene-cyanophosphinidene adducts **8**·PCN ( $\delta^{31}\text{P} = -133$ ) and **18**·PCN ( $\delta^{31}\text{P} = -38$ ) can be obtained by reacting [**8**-Cl][BF<sub>4</sub>] and [**18**-Cl][BF<sub>4</sub>] with [18]crown-6-sodium dicyanophosphide followed by reduction with sodium diethylphosphite (Scheme 15).<sup>[4]</sup> 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<sub>pπ</sub>–C<sub>pπ</sub> 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.

Another effective route to NHC-phosphinidene adducts was developed by Grützmacher and co-workers, who employed sodium phosphoethynolate, 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

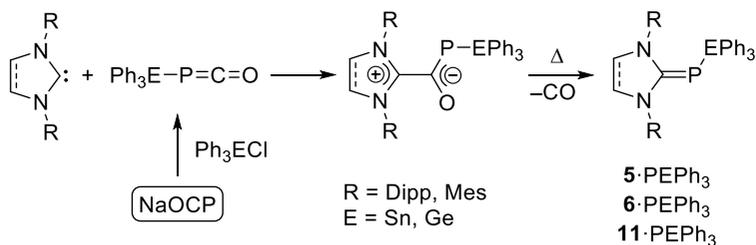
work-up **6**·PH ( $\delta^{31}\text{P} = -136.7$ ) in 71% yield (Scheme 16).<sup>[22]</sup> Analogously, the parent phosphinidene adducts **7**·PH (87%;  $\delta^{31}\text{P} = -134.5$ )<sup>[27]</sup> and **10**·PH (34.5%;  $\delta^{31}\text{P} = -127.2$ )<sup>[28]</sup> were prepared (Scheme 16), yet this method does not tolerate N-alkylated imidazolium salts, such as **[1-H][Cl]** and **[3-H][Cl]**.<sup>[37]</sup>



**Scheme 16.** Synthesis of carbene-phosphinidene adducts by phosphide transfer reactions from Na(OCP).

### 1.2.6. Phosphaketenes

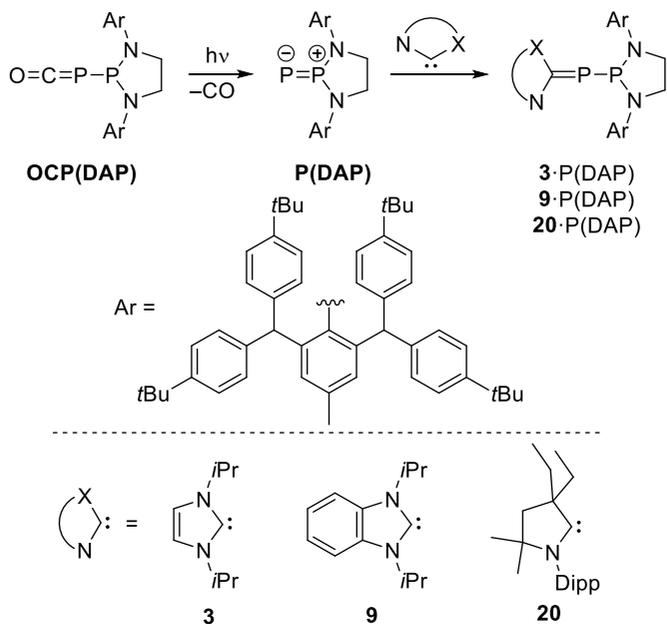
For the synthesis of substituted phosphinidene adducts, Na(OCP) can also be used to prepare tetrel substituted phosphaketenes, such as  $\text{Ph}_3\text{Sn}(\text{PCO})$  and  $\text{Ph}_3\text{Ge}(\text{PCO})$ .<sup>[38]</sup> These phosphaketenes react with NHCs **5**, **6** and **11** to form the corresponding NHC-phosphaketene adducts that decompose upon thermolysis under the release of carbon monoxide to afford NHC-phosphinidene adducts (**5**, **6**, **11**)·PEPh<sub>3</sub> (E = Sn, Ge) almost quantitatively (Scheme 17).<sup>[20]</sup>



**Scheme 17.** Carbene-phosphinidene adduct synthesis from NHC-phosphaketene adducts.

### 1.2.7. Phosphinidenes

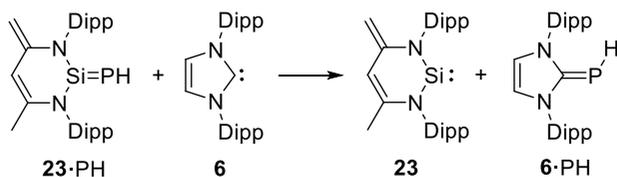
Sterically encumbered phosphaketenes can also be decarbonylated prior to the addition of N-heterocyclic carbenes. Bertrand and co-workers have isolated a room-temperature stable, monomeric (phosphino)phosphinidene (**P(DAP)**), by photolysis of the corresponding (phosphino)phosphaketene (**OCP(DAP)**) (Scheme 18).<sup>[39]</sup> 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);  $\delta^{31}\text{P} = 76.3$ ) and less electrophilic carbenes such as imidazol-2-ylidene **3** (**3**·P(DAP);  $\delta^{31}\text{P} = -68.2$ ) and benzimidazol-2-ylidene **9** (**9**·P(DAP);  $\delta^{31}\text{P} = -35.5$ ) have been prepared (Scheme 18), illustrating the electrophilic nature of this phosphinidene.<sup>[17]</sup>



**Scheme 18.** Synthesis of carbene-phosphinidene adducts by phosphinidene addition to carbenes. DAP = 1,3-bis-Ar-1,3,2-diazaphospholide.

### 1.2.8. Phosphinidene Transfer

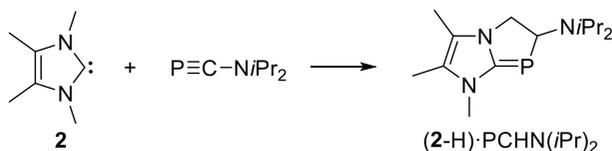
For thermally unstable phosphinidenes, Driess and co-workers developed a phosphinidene transfer reaction. Phoshasilene **23**·PH ( $\delta^{31}\text{P} = -293.9$ ) features a highly polarized Si–P bond, which enables transfer of the parent phosphinidene, [PH], at room temperature to *N*-heterocyclic carbene **6** to quantitatively afford **6**·PH ( $\delta^{31}\text{P} = -136.7$ ) and silylene **23** (Scheme 19).<sup>[21]</sup>



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

### 1.2.9. Phosphaalkynes

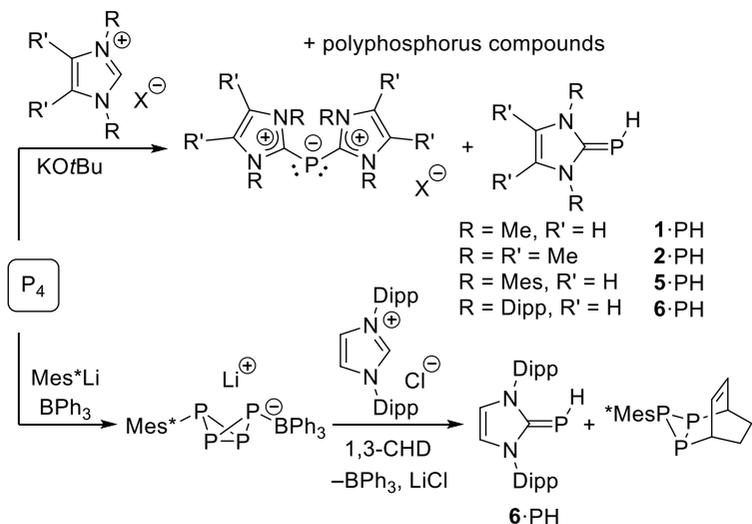
The only example of using phosphaalkynes to produce NHC-phosphinidene adducts comes from Hahn *et al.*, who synthesized the bicyclic adduct (2-H)·PCHN(*i*Pr)<sub>2</sub> ( $\delta^{31}\text{P} = -64.8$ ) in almost quantitative yield from aminophosphaalkyne *i*Pr<sub>2</sub>NCP and N-heterocyclic carbene **2** (Scheme 20).<sup>[11]</sup> To date, this remains the only example of an intramolecular carbene-stabilized phosphinidene.



**Scheme 20.** Synthesis of the intramolecular carbene-stabilized phosphinidene adduct (2-H)·PCHN(*i*Pr)<sub>2</sub> from a phosphaalkyne and **2**.

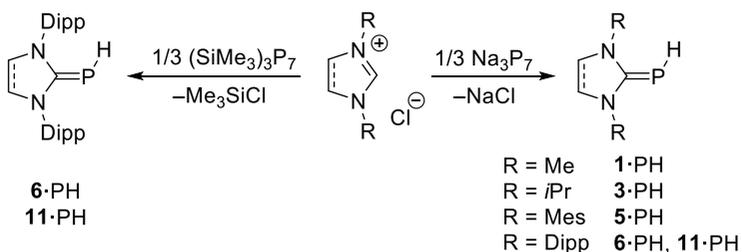
### 1.2.10. Polyphosphorus compounds

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<sub>4</sub>) with *in situ* generated carbenes, from imidazolium salts and KO<sup>t</sup>Bu, to produce (1, 2, 5, 6)·PH adducts together with bis(NHC)-stabilized phosphorus cations and some unidentified polyphosphorus compounds (Scheme 21).<sup>[8]</sup> 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<sub>4</sub> was functionalized with the bulky Mes\*Li (Mes\* = 2,4,6-*t*Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) and BPh<sub>3</sub> to give the borane-stabilized bicyclo[1.1.0]tetraphosphabutane anion Mes\*P<sub>4</sub><sup>-</sup>, which through selective [3+1] fragmentation using imidazolium chloride [6-H][Cl] afforded 6·PH, while the P<sub>3</sub>-unit was trapped with 1,3-cyclohexadiene (Scheme 21).<sup>[40]</sup>



**Scheme 21.** Preparation of carbene-phosphenidene adducts from elemental phosphorus. X = Cl or I, Mes\* = 2,4,6-*t*Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, CHD = cyclohexadiene.

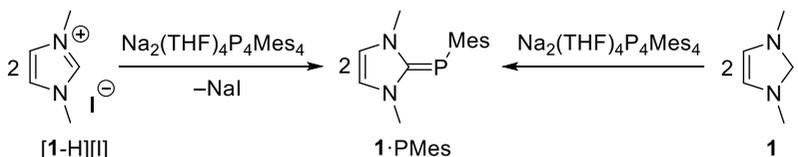
The heptaphosphides Na<sub>3</sub>P<sub>7</sub> and (Me<sub>3</sub>Si)<sub>3</sub>P<sub>7</sub> can be easily obtained from P<sub>4</sub> and P<sub>red</sub>, and are versatile precursors for the synthesis of carbene-phosphenidene adducts.<sup>[8]</sup> Grützmacher and co-workers demonstrated that (dihydro)imidazolium chlorides react with Na<sub>3</sub>P<sub>7</sub><sup>[8]</sup> or (Me<sub>3</sub>Si)<sub>3</sub>P<sub>7</sub><sup>[22,29]</sup> resulting in phosphenidene 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<sub>2</sub>(THF)<sub>4</sub>P<sub>4</sub>Mes<sub>4</sub>) is a convenient precursor for

mesitylphosphinidene adducts. Treating  $\text{Na}_2(\text{THF})_4\text{P}_4\text{Mes}_4$  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 ( $\delta^{31}\text{P} = -73.8$ ; Scheme 23).<sup>[10]</sup>



**Scheme 23.** Synthesis of **1**·PMes from  $\text{Na}_2(\text{THF})_4\text{P}_4\text{Mes}_4$ .

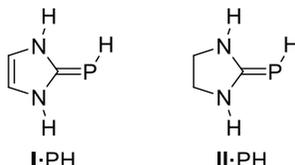
### 1.3. Structure and Bonding

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.

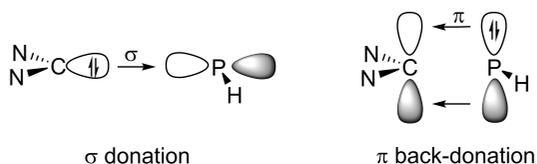
#### 1.3.1. Theoretical Studies

Generally, the electronic properties of C-amino substituted phosphalkenes differ significantly from the classical C-substituted phosphalkenes  $\text{R}^1\text{R}^2\text{C}=\text{PR}^3$ . 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 ( $\text{P}^{\delta-}-\text{C}^{\delta+}$ ).<sup>[5a]</sup> 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),<sup>[41]</sup> 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

(Scheme 25).<sup>[41b]</sup> 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.<sup>[41a]</sup>



**Scheme 24.** Model compounds used for DFT calculations by Frison and Sevin.



**Scheme 25.** Schematic representation of the dominant orbital interactions forming the central C–P bond.

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  $P_{p\pi}$ – $C_{p\pi}$  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.<sup>[41c]</sup> 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**·P(SiCl<sub>2</sub>L) features a classical double bond.<sup>[33]</sup>

Several other computational studies on NHC-phosphinidene adducts confirmed that polarization of the P–C  $\pi$ -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**·PPh and found that the P–C  $\pi$ -bond is significantly polarized towards phosphorus (60.7%), while the  $\sigma$ -bond is polarized towards the carbene carbon (66.5%).<sup>[24]</sup> The anionic NHC–parent phosphinidene adduct Li·I·PH features an even more P-localized P–C  $\pi$ -bond (71.2% P and 28.5% C) and C-localized  $\sigma$ -bond (65.7% C and 34.3% P).<sup>[26]</sup> Phosphinidene adducts of monoamidocarbene **13**·PPh and CAACs **21**·PPh,<sup>[30]</sup> *E*-**19**·PCl<sup>[31]</sup> and **19**·P(SiL)<sup>[33]</sup> also feature P-polarized  $\pi$ -bonds (60.0%, 60.3%, 59.5% and 59.0% at P, respectively). In contrast, diamidocarbene-phenylphosphinidene adducts **12**·PPh and **14**·PPh<sup>[30]</sup> and *Z*-isomer of CAAC-chlorophosphinidene adduct *Z*-**19**·PCl<sup>[31]</sup> are characterized by a more developed  $\pi$ -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 phosphalkene resonance structure **A** (). Additionally, the Wiberg bond indexes (WBI) indicate that **12**·PPh, **14**·PPh (WBI for the P atom, including two  $\sigma$  and one  $\pi$ -bond, are 2.91 and 2.90)<sup>[30]</sup> and *Z*-**19**·PCl (WBI of the P–C bond is 1.626)<sup>[31]</sup> have a higher double-bond character than **19**·P(SiL), **19**·P(SiCl<sub>2</sub>L),<sup>[33]</sup> **6**·PH<sup>[21]</sup> and *E*-**19**·PCl<sup>[31]</sup> (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 <sup>31</sup>P NMR chemical shifts (between  $\delta^{31}\text{P} = -179.5$  ppm for **5**·PSnPh<sub>3</sub><sup>[20]</sup> and  $\delta = 163.4$  ppm for *E*-**21**·PCl,<sup>[31]</sup> see Table 1), compared to those of classical phosphalkenes ( $\delta^{31}\text{P} = 230\text{--}420$  ppm).<sup>[42]</sup> For NHC=PPh adducts, Bertrand and co-workers showed

that the  $^{31}\text{P}$  NMR chemical shifts can be used as indicator to evaluate the relative  $\pi$ -accepting properties of carbenes.<sup>[15]</sup> 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  $^{31}\text{P}$  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  $^{31}\text{P}$  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.

$^1\text{H}$  and  $^{13}\text{C}$  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  $^1\text{H}$  and  $^{13}\text{C}$  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  $\Delta G^\ddagger = 34 \text{ kJ mol}^{-1}$  for **6**·PPh and  $\Delta G^\ddagger = 58 \text{ kJ mol}^{-1}$  for **11**·PPh.<sup>[15]</sup> Furthermore, the (**12–14**)·PPh adducts bearing the strongly  $\pi$ -accepting carbonyl-decorated carbenes **12–14** exhibit more downfield  $^{31}\text{P}$  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  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra in solution at room temperature.<sup>[30]</sup>

The nature of the phosphorus substituent on the NHC=PR adducts also has a significant influence on the  $^{31}\text{P}$  chemical shift. As predicted by DFT calculations,<sup>[41c]</sup> electron-withdrawing substituents (e.g., Ph, Mes) result in more downfield  $^{31}\text{P}$  NMR shifts, whereas electron-donating groups (e.g., SiMe<sub>3</sub>, GePh<sub>3</sub>, SnPh<sub>3</sub>) lead to more upfield shifts. Indeed, the  $^{31}\text{P}$  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**·PGePh<sub>3</sub> (−145.1 ppm) and **6**·PSnPh<sub>3</sub> (−161.5 ppm), have more upfield shifts. This is in agreement with decreasing electron-withdrawing ability in the series Ph > Mes > H > GePh<sub>3</sub> > SnPh<sub>3</sub>.

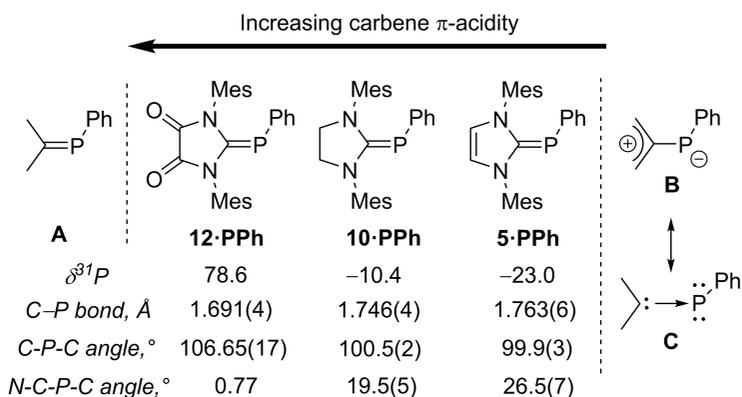
Another important factor influencing the <sup>31</sup>P NMR chemical shift is the stereochemistry around the P=C bond. For amino-substituted phosphalkenes (phosphaamidenes) it was found that the *E*-isomers display more downfield <sup>31</sup>P NMR chemical shifts than the *Z*-isomers.<sup>[43,7a]</sup>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

The <sup>13</sup>C 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 phosphalkenes (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  $\pi$ -acidity of the carbene (e.g., **12**) leads to a shorter P–C bond, while weakly  $\pi$ -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  $\pi$ -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  $^{31}P$  NMR chemical shift and selected structural parameters of NHC-phosphinidene adducts with the same P substituent.

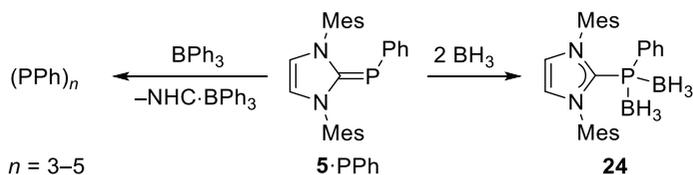
## 1.4. Reactivity of N-heterocyclic Carbene-Phosphinidene Adducts

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.

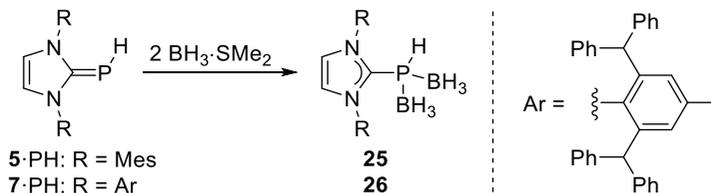
### 1.4.1. Addition reactions with main-group and organic compounds

*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 ( $\delta^{31}\text{P} = -23.0$ ) with two equivalents of  $\text{BH}_3\cdot\text{THF}$  resulted exclusively in bis(borane) adduct **24** (73%,  $\delta^{31}\text{P} = 4.0$ ; 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.<sup>[44]</sup> Interestingly, the more sterically demanding Lewis acid  $\text{BPh}_3$  induces formation of cyclopolyphosphines  $(\text{PPh})_n$  ( $n = 3-5$ ; Scheme 27), which precludes the possibility of developing phosphinidene transfer reactions (see 1.4.5). The  $\text{BH}_3$  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  $\text{PAr}_3$  (Ar =  $\text{C}_6\text{H}_2(\text{OMe})_3-2,4,6$ ). Arduengo *et al.* also probed for the first time the redox chemistry of  $\text{NHC}=\text{PR}$  adducts by means of cyclic voltammetry and established that **5**·PPh undergoes facile one-electron oxidation at  $-0.08$  V (vs. SCE).



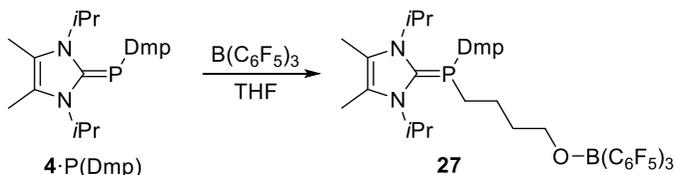
**Scheme 27.** Reactions of **5**·PPh with  $\text{BH}_3$  and  $\text{BPh}_3$ .

Following a similar protocol, the groups of von Hänisch, Bertrand and Hahn showed that, respectively, **5**·PH,<sup>[18]</sup> **7**·PH,<sup>[27]</sup> and **(2-H)**·PCHN(iPr)<sub>2</sub><sup>[11]</sup> react with two equivalents of  $\text{BH}_3\cdot\text{THF}$  or  $\text{BH}_3\cdot\text{SMe}_2$  to form the corresponding bis(borane) adducts **25**, **26** and **30** (Scheme 28 and Scheme 32).



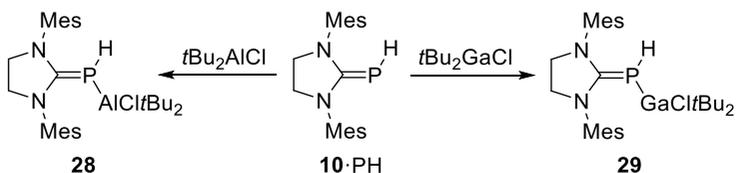
**Scheme 28.** Reactions of 5-PH and 7-PH with  $\text{BH}_3$ .

Ragogna and co-workers reacted **4**·P(Dmp) ( $\delta^{31}\text{P} = -75.0$ ) with the strongly Lewis acidic  $\text{B}(\text{C}_6\text{F}_5)_3$  in THF, which results in controlled ring-opening of THF affording product **27** ( $\delta^{31}\text{P} = -24.7$ ; Scheme 29).<sup>[13]</sup>



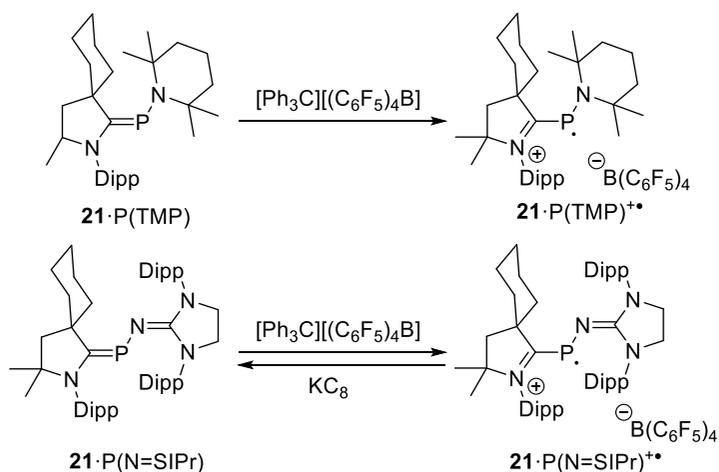
**Scheme 29.** Reaction of **4**·P(Dmp) with  $\text{B}(\text{C}_6\text{F}_5)_3$  in THF. Dmp = 2,6-dimesitylphenyl.

In contrast to the parent borane, treatment of **10**·PH ( $\delta^{31}\text{P} = -127.2$ ) with the bulkier Lewis acids  $t\text{Bu}_2\text{AlCl}$  and  $t\text{Bu}_2\text{GaCl}$  gave mono(alane) and mono(galane) adducts **28** ( $\delta^{31}\text{P} = -151.0$ ) and **29** ( $\delta^{31}\text{P} = -148.8$ ; Scheme 30).<sup>[28]</sup> 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).<sup>[28]</sup>



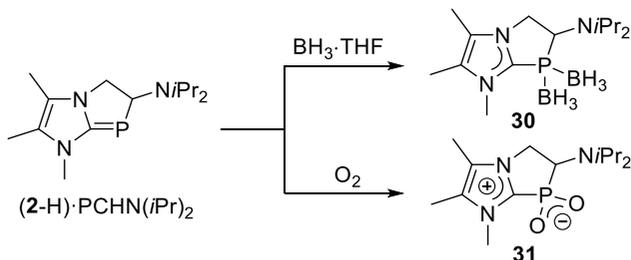
**Scheme 30.** Reactions of **10**·PH with  $t\text{Bu}_2\text{AlCl}$  and  $t\text{Bu}_2\text{GaCl}$ .

*Oxidation.* Stimulated by Arduengo's earlier results, Bertrand and co-workers investigated the redox chemistry of CAAC-phosphinidene adducts  $\mathbf{21}\cdot\text{P}(\text{TMP})^{[34]}$  and  $\mathbf{21}\cdot\text{P}(\text{N}=\text{SIPr})^{[35]}$  with  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ , which resulted in one-electron oxidation affording the thermally stable radical cations  $\mathbf{21}\cdot\text{P}(\text{TMP})^{+\bullet}$  and  $\mathbf{21}\cdot\text{P}(\text{N}=\text{SIPr})^{+\bullet}$  that display significant spin density on the phosphorus atom (0.67e and 0.40e, respectively), as determined by DFT calculations. Addition of  $\text{KC}_8$  to a toluene solution of  $\mathbf{21}\cdot\text{P}(\text{N}=\text{SIPr})^{+\bullet}$  resulted in reformation of the neutral  $\mathbf{21}\cdot\text{P}(\text{N}=\text{SIPr})$  by one-electron reduction, thus illustrating a fully reversible redox system (Scheme 31).<sup>[35]</sup>



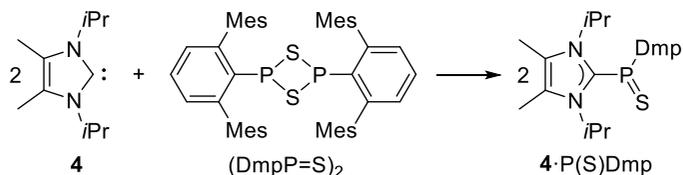
**Scheme 31.** Redox chemistry of CAAC-phosphinidene adducts.

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



**Scheme 32.** Reactions of  $(2\text{-H})\cdot\text{PCHN}(\text{iPr})_2$  with  $\text{BH}_3$  and air.

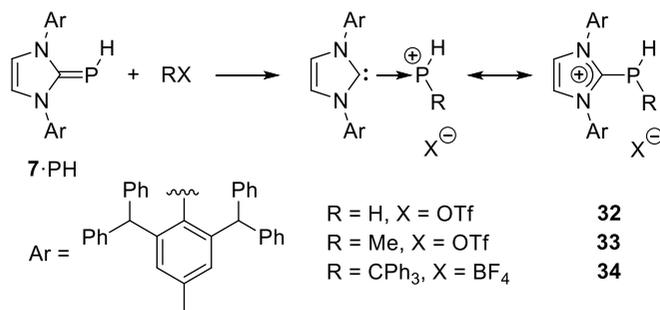
To date no NHC-stabilized mono(phosphenidene)oxides have been reported, yet the related base-stabilized phosphenidene sulfide became very recently available. Ragogna and co-workers treated the dimeric phosphenidene sulfide  $(\text{DmpP}=\text{S})_2$  ( $\delta^{31}\text{P} = 124$ ) with two equivalents of 1,3-di-*iso*-propyl-4,5-dimethylimidazol-2-ylidene (**4**) at room temperature to afford the first monomeric phosphenidene sulfide  $4\cdot\text{P}(\text{S})\text{Dmp}$  ( $\delta^{31}\text{P} = 29$ ; Scheme 33).<sup>[45]</sup>



**Scheme 33.** Synthesis of a NHC-stabilized phosphenidene sulfide.

*Protonation and alkylation.* Next to neutral Lewis acids and oxidants, the reactivity of  $\text{NHC}=\text{PR}$  adducts has also been studied towards cationic electrophiles. Bertrand and co-workers have demonstrated that the sterically encumbered parent phosphenidene adduct  $7\cdot\text{PH}$  can be protonated and alkylated at the phosphorus atom. Addition of trifluoromethanesulfonic acid (HOTf) to a benzene solution of  $7\cdot\text{PH}$  ( $\delta^{31}\text{P} = -134.5$ ) afforded the NHC-stabilized parent phosphonium salt **32** (85%,  $\delta^{31}\text{P} = -166.6$ ; Scheme 34), while alkylation was achieved by treatment of  $7\cdot\text{PH}$  with methyl trifluoromethanesulfonate ( $\text{MeOTf}$ ) and  $[\text{Ph}_3\text{C}][\text{BF}_4]$  resulting in

NHC-stabilized phosphonium salts **33** (87%,  $\delta^{31}\text{P} = -86.3$ ) and **34** (89%,  $\delta^{31}\text{P} = -49.4$ ), respectively (Scheme 34).<sup>[27]</sup>

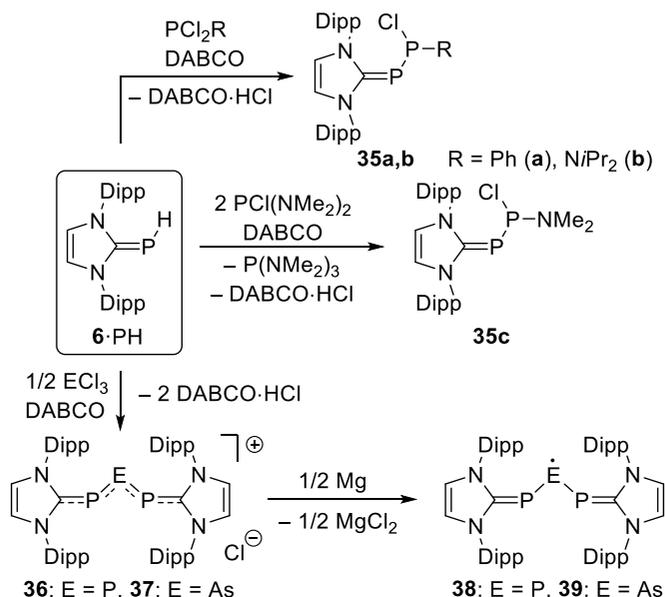


**Scheme 34.** Protonation and alkylation reactions of **7-PH**.

#### 1.4.2. Substitution reactions with main-group and organic compounds

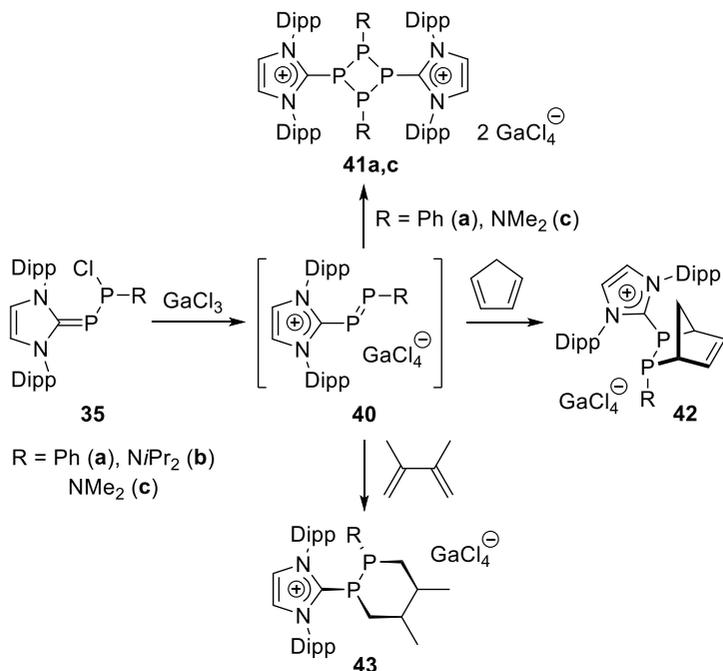
Apart from functioning as a strong Lewis base (see Section 1.4.1), PH- and PCI-functionalized N-heterocyclic carbene phosphinidene adducts can also undergo substitution reactions at the phosphorus center offering an alternative approach to create functionalized NHC=PR adducts. For example, Grützmacher and co-workers showed that the parent phosphinidene-carbene adduct **6-PH** ( $\delta^{31}\text{P} = -136.7$ ) reacts with dichlorophosphines  $\text{PCl}_2\text{R}$  in the presence of the non-nucleophilic base DABCO (1,4-diazabicyclo[2.2.2]octane) to yield the neutral species **6-PPCIR** **35** ( $\text{R} = \text{Ph}$  (**a**);  $\delta^{31}\text{P} = -17.3$ ) or  $\text{NiPr}_2$  (**b**);  $\delta^{31}\text{P} = -18.4$ ); see Scheme 35).<sup>[25]</sup> However, treatment of **6-PH** with chlorobis(dimethylamino)phosphine does not afford **6-PP(NMe<sub>2</sub>)<sub>2</sub>**, but **6-PPCINMe<sub>2</sub>** **35c** ( $\delta^{31}\text{P} = -33.5$ ) and  $\text{P(NMe}_2)_3$  as a second equivalent of  $\text{PCl(NMe}_2)_2$  acts as chloride donor (Scheme 35).<sup>[25]</sup> The pnictogen chlorides  $\text{ECl}_3$  (0.5 equiv;  $\text{E} = \text{P}, \text{As}$ ) 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  $\text{P}_3$  and  $\text{PAsP}$  cations **36** ( $\delta^{31}\text{P} = 190.6$  ( $\text{P}=\text{C}$ ), 591.9), **37** ( $\delta^{31}\text{P} = 218.9$ ) (Scheme 35).<sup>[22]</sup> 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 P<sub>3</sub> transfer (see Section 1.4.5 and Scheme 51).<sup>[22]</sup>



**Scheme 35.** Reactions of **6-PH** with pnictogen chlorides. DABCO = 1,4-diazabicyclo[2.2.2]octane.

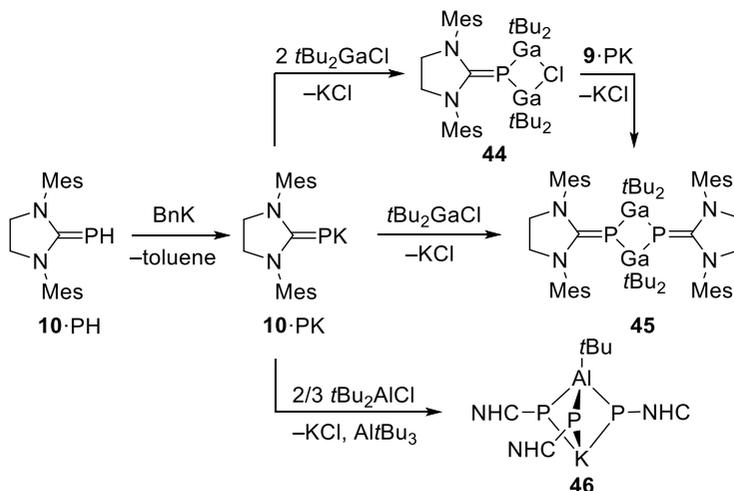
Chlorophosphines **35** offer interesting follow-up chemistry. Namely, treatment of **35** with gallium trichloride resulted in chloride abstraction and the formation of the corresponding cationic diphosphenes  $[\text{6}\cdot\text{P}=\text{PR}]^+$  **40**, which depending on the steric bulk of the R 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).<sup>[25]</sup>



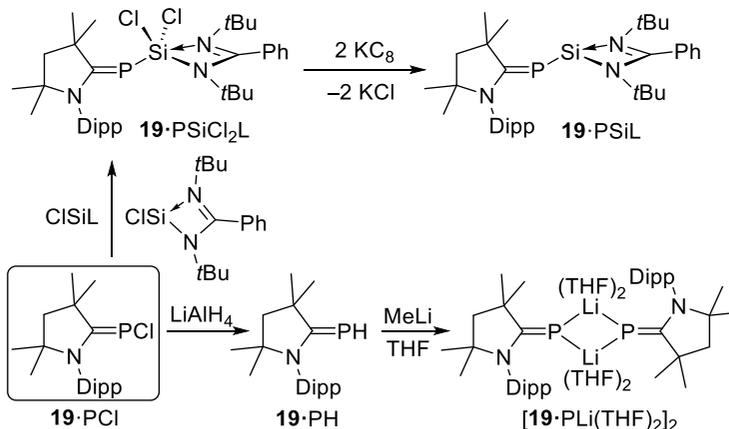
**Scheme 36.** Chloride abstraction reactions of **35** with  $\text{GaCl}_3$  both in the presence and absence of trapping agents.

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  $t\text{Bu}_2\text{MCl}$  ( $\text{M} = \text{Al}, \text{Ga}$ ) affording aluminum and gallium phosphinidenyl complexes **44–46** (Scheme 37).<sup>[28]</sup>

Frenking, Stalke, Roesky and co-workers have reported on the functionalization of chlorophosphinidene adduct **19**·PCI ( $\delta^{31}\text{P} = 161.9/129.4$ ), which oxidatively adds to chlorosilylene  $\text{LSiCl}$  ( $\text{L} = \text{benzamidinate}$ ) affording dichlorosilane **19**·PSiCl<sub>2</sub>L (84%,  $\delta^{31}\text{P} = 59.0$ ) that upon reduction with two equivalents of potassium graphite generated the CAAC-stabilized silylene-phosphinidene **19**·PSiL (67%,  $\delta^{31}\text{P} = 68.8$ ; Scheme 38).<sup>[33]</sup> Reduction of chlorophosphinidene adduct **19**·PCI with  $\text{LiAlH}_4$  affords the parent phosphinidene-CAAC adduct **19**·PH (70%,  $\delta^{31}\text{P} = -38.4/-44.9$ ),<sup>[31]</sup> which upon lithiation with MeLi in THF gives lithium phosphinidenyl [**19**·PLi(THF)<sub>2</sub>]<sub>2</sub> (65%,  $\delta^{31}\text{P} = 177.3$ ; Scheme 38).<sup>[32]</sup>



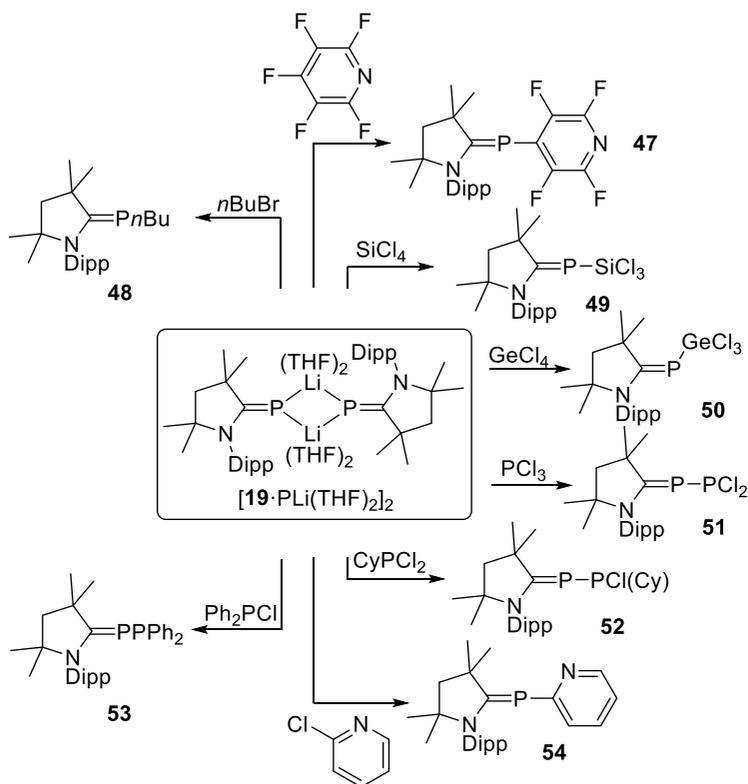
**Scheme 37.** Synthesis of aluminium(III) and gallium(III) phosphinidenyl complexes. Bn = benzyl, NHC = **10**.



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

Lithium phosphinidenyl  $[\mathbf{19}\cdot\text{PLi}(\text{THF})_2]_2$  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**(*p*- $\text{C}_6\text{F}_4\text{N}$ ) (**47**; 71%,  $\delta^{31}\text{P} = -4.3$ ), **19·P***n*Bu (**48**; 79%,  $\delta^{31}\text{P} = 61.2$ ), **19·P**(*o*-Py) (**54**; 68%,  $\delta^{31}\text{P} = 65.4$ )), P–Si (**19·PSiCl**<sub>3</sub> (**49**; 67%,  $\delta^{31}\text{P} = -22.0$ ), P–Ge (**19·PGeCl**<sub>3</sub> (**50**;

85%,  $\delta^{31}\text{P} = 47.8$ ) and P–P bonds (**19**·PPCl<sub>2</sub> (**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<sub>2</sub> (**53**; 80%,  $\delta^{31}\text{P} = 41.2, -27.3$ ; see Scheme 39).<sup>[32]</sup>

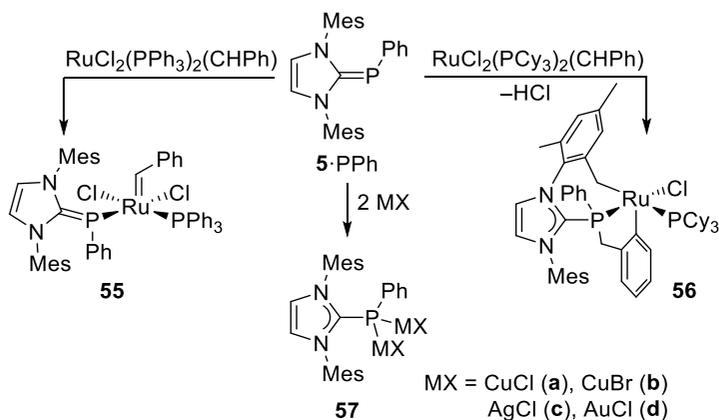


**Scheme 39.** Reactions of base-stabilized phosphorus atom with organic and inorganic substrates. Cy = Cyclohexyl.

### 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

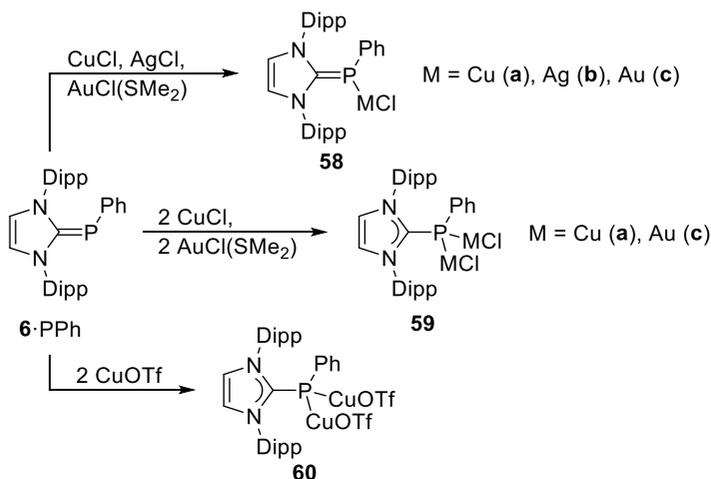
and Lavoie in 2014, who reacted **5**-PPh with Grubbs first-generation ruthenium benzylidene complexes.<sup>[46]</sup> Addition of **5**-PPh (1 equiv) to RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(CHPh) resulted in ligand exchange and the formation of η<sup>1</sup>-coordination product **55**, which was, however, inactive in ring-opening metathesis of diallyl sulfide. The use of RuCl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>(CHPh) did not afford RuCl<sub>2</sub>(**5**-PPh)(PCy<sub>3</sub>)(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.

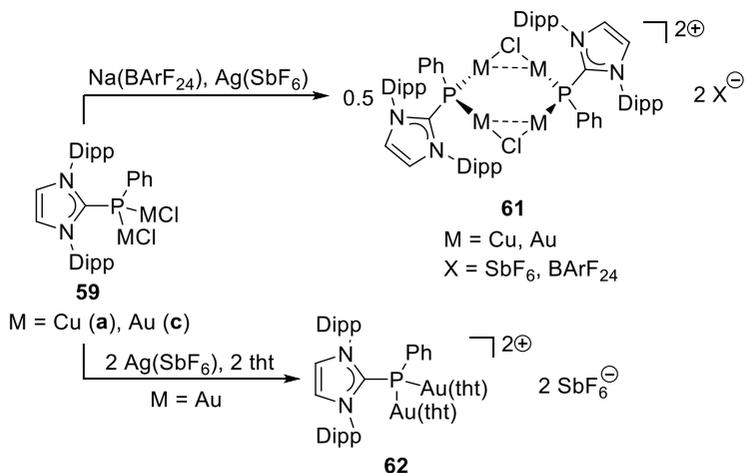
Dias and co-workers explored the coordination chemistry of **5**-PPh towards coinage metals and prepared the bimetallic coinage metal complexes **57** (Scheme 40).<sup>[47]</sup> While copper(I) and silver(I) adducts **57a–c** crystallized as halide ion bridged octanuclear complexes, bis-gold(I) chloride 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).<sup>[24]</sup> Depending on the stoichiometry of the reactions with CuCl and AuCl(SMe<sub>2</sub>), 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.



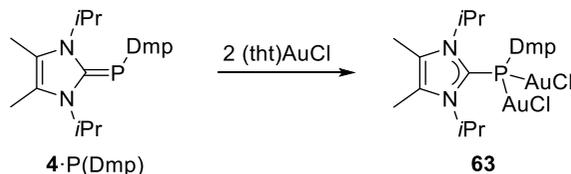
**Scheme 41.** Synthesis of coinage metal complexes of **6-PPh**.

Subsequent treatment of the bimetallic complexes **59** (M = Cu, Au) with chloride abstraction reagents (NaBARF<sub>24</sub> or AgSbF<sub>6</sub>) gave the dicationic 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).<sup>[24]</sup> Complete chloride abstraction was observed by reacting **59c** with two equivalents of AgSbF<sub>6</sub> in the presence of tetrahydrothiophene (tht), which afforded complex **62**. Both gold species **61** and **62** were employed as catalysts for 1,6-enyne cyclization and carbene transfer reactions using diethyl diazoacetate, thereby illustrating for the first time the application of NHC-phosphinidene complexes in homogeneous catalysis.



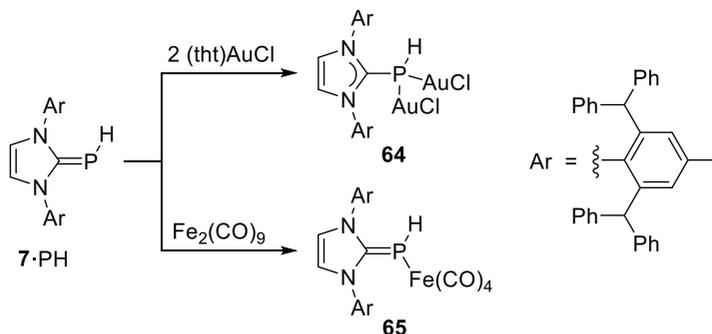
**Scheme 42.** Synthesis of cationic copper(I) and gold(I) complexes. tht = tetrahydrothiophene.

Ragogna and co-workers explored the coordination of (tht)AuCl to  $4\text{-P}(\text{Dmp})$  ( $\delta^{31}\text{P} = -75.0$ ). This reaction resulted in the formation of bis-gold(I) chloride complex **63** ( $\delta^{31}\text{P} = -41.9$ ; Scheme 43) which akin to **59c** is monomeric in the solid state.<sup>[13]</sup>



**Scheme 43.** Reaction of  $4\text{-P}(\text{Dmp})$  with (tetrahydrothiophene)gold(I) chloride. Dmp = 2,6-dimesitylphenyl, tht = tetrahydrothiophene.

Bertrand and co-workers have demonstrated that also the parent carbene-phosphinidene adduct  $7\text{-PH}$  reacts with two equivalents of (tht)AuCl resulting in bis-metal complex **64** (Scheme 44).<sup>[27]</sup> In contrast, treatment of  $7\text{-PH}$  with diiron nonacarbonyl led to mono-iron complex **65**, due to steric constraints as the addition of excess  $[\text{Fe}_2(\text{CO})_9]$  did not lead to further coordination.

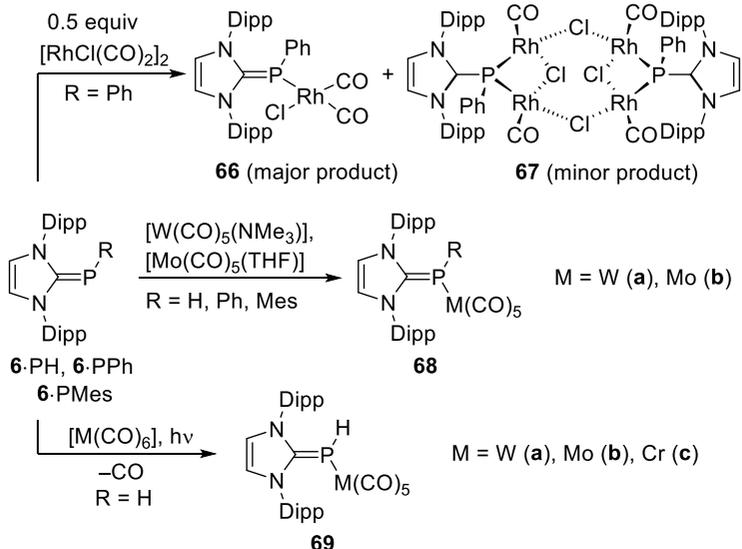


**Scheme 44.** Reactions of **7-PH** with (tetrahydrothiophene)gold(I) chloride and diiron nonacarbonyl. tht = tetrahydrothiophene.

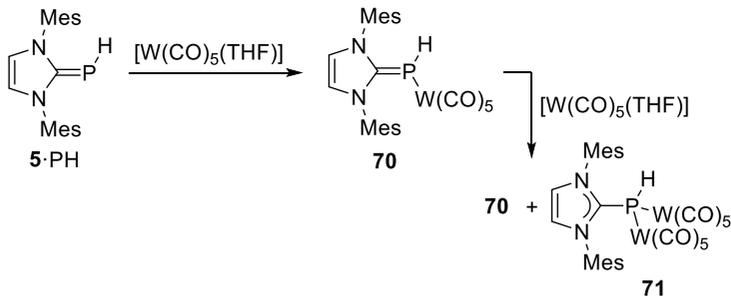
To probe the P-donor properties of the NHC=PR adducts, Tamm and co-workers reacted **6-PR** (R = H, Ph, Mes) with the metal carbonyl complexes  $[\text{Rh}(\mu\text{-Cl})(\text{CO})_2]_2$ ,  $[\text{W}(\text{CO})_5(\text{NMe}_3)]$  and  $[\text{Mo}(\text{CO})_5(\text{THF})]$  to afford dicarbonyl rhodium(I) complex **66**, tetranuclear complex **67**, and tungsten and molybdenum pentacarbonyl complexes **68** (M = Mo, W), respectively (Scheme 45).<sup>[48]</sup> 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 carbodienes, also bearing two lone pairs on the donor atom, were observed.<sup>[49]</sup>

NHC=PR carbonyl complexes **69** of the group 6 transition metals can also be prepared directly from the metal hexacarbonyls  $[\text{M}(\text{CO})_6]$  (M = W, Mo, Cr) using UV light, as was shown by Bispinghoff and Grützmacher for **6-PH** (Scheme 45).<sup>[37]</sup> 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  $[\text{W}(\text{CO})_5(\text{THF})]$  to **5-PH** afforded monometallic **70**, which upon addition of an excess of  $[\text{W}(\text{CO})_5(\text{THF})]$  led to a mixture of **70** and bimetallic **71** that was spectroscopically characterized (Scheme 46).<sup>[18]</sup> Interestingly, these carbonyl complexes mimic carbene adducts of the

transient electrophilic phosphinidenes  $[RP=M(CO)_5]$ , such as  $[(2\text{-}PR)W(CO)_5]$  ( $R = CH(SiMe_3)_2$ ) that was prepared by Streubel and co-workers.<sup>[50]</sup>



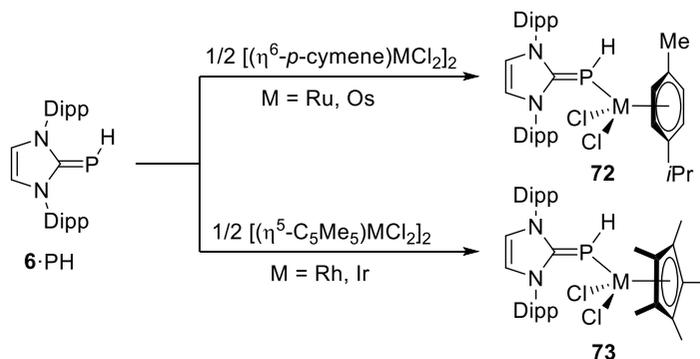
**Scheme 45.** Synthesis of transition metal carbonyl complexes of carbene-phosphinidene adducts **6·PH**, **6·PPh** and **6·PMes**.



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

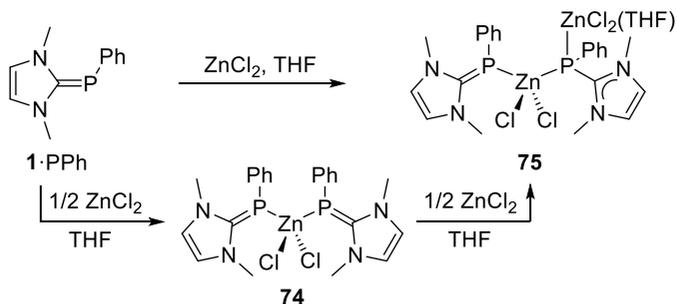
The reactivity of carbene-phosphinidene adduct **6·PH** towards group 8 and 9 metal complexes has been investigated by Tamm and co-workers (Scheme 47). Addition of dimeric complexes of the type  $[LMCl_2]_2$  ( $M = Ru, Os, Rh, Ir$ ) to **6·PH** afforded the three-legged piano-stool complexes  $[(6\text{-}PH)_3M(L)Cl_2]$  **72** ( $M = Ru/Os, L$

=  $\eta^6$ -*p*-cymene) and **73** (M = Rh/Ir, L =  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>), which upon dehydrochlorination with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) can partly be converted into the corresponding NHC-phosphinidene complexes **76** and **77** (see 1.4.4 and Scheme 49).<sup>[51]</sup>



**Scheme 47.** Reactions of carbene-phosphinidene adduct **6·PH** with ruthenium(II), osmium(II), rhodium(III) and iridium(III) complexes.

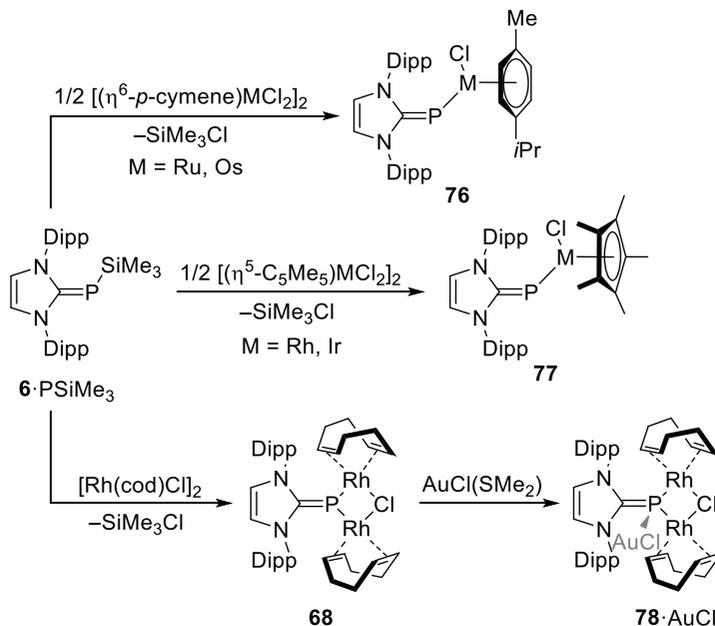
Slootweg, Grützmacher and co-workers explored the reactivity of carbene-phosphinidene adduct **1·PPh** towards ZnCl<sub>2</sub> (Scheme 48). Namely, reaction of **1·PPh** with half an equivalent of ZnCl<sub>2</sub> led to bis(**1·PPh**) zinc complex **74**, which upon addition of another half equivalent of ZnCl<sub>2</sub> afforded the 1:1 zinc carbene-phosphinidene complex **75**.<sup>[9]</sup> The latter can also be obtained directly by treating **1·PPh** with one equivalent of ZnCl<sub>2</sub>. Interestingly, ZnCl<sub>2</sub> complexation of NHC-phosphinidene adduct **1·PPh** induced selective phenylphosphinidene transfer reactions to electron-poor heterodienes (see 1.4.5 and Scheme 53).



**Scheme 48.** Synthesis of ZnCl<sub>2</sub> complexes of carbene-phosphinidene adduct 1·PPh.

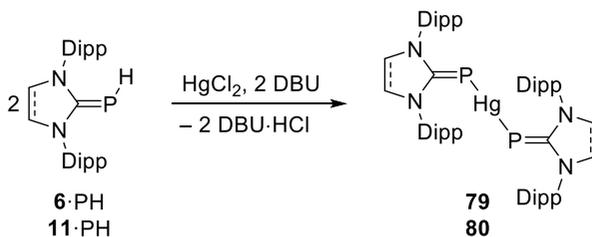
#### 1.4.4. Substitution reactions with transition-metal complexes

Besides complexation, NHC=PH and NHC=Psilyl adducts can undergo substitution reactions with transition-metal halides. Tamm and co-workers reacted **6**·PSiMe<sub>3</sub> with the dinuclear metal halides [LMCl<sub>2</sub>]<sub>2</sub> (M = Ru/Os, L = η<sup>6</sup>-*p*-cymene; M = Rh/Ir, L = η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>) and [Rh(cod)Cl]<sub>2</sub> to afford, after elimination of trimethylsilyl chloride, the NHC-phosphinidene 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).<sup>[23,51]</sup> Complexes **76–78** can be reacted further with AuCl(SMe<sub>2</sub>) to yield bimetallic complexes **76**·AuCl, **77**·AuCl and trimetallic complex **78**·AuCl (see Scheme 49) with three- and four-coordinated phosphorus atoms, respectively.<sup>[23]</sup>



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

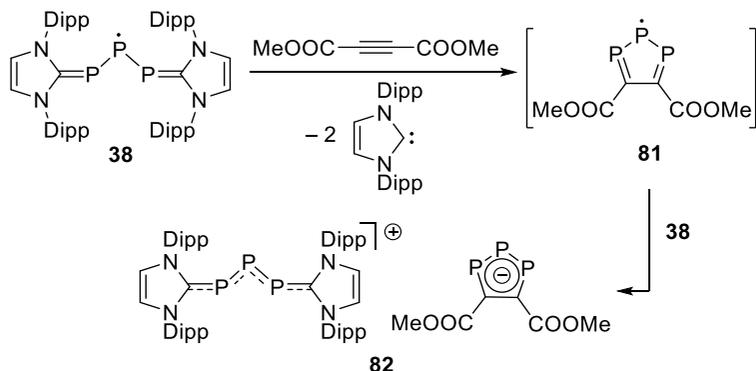
Grützmacher, Pringle and co-workers have demonstrated that the parent NHC=PHs **6·PH** and **11·PH** can be converted into the corresponding linear bis(carbene-phosphinidenyl) Hg complexes **79** and **80** by treatment with half an equivalent of mercury(II) chloride in the presence of DBU (Scheme 50).<sup>[29]</sup>



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

### 1.4.5. Phosphinidene transfer reactions

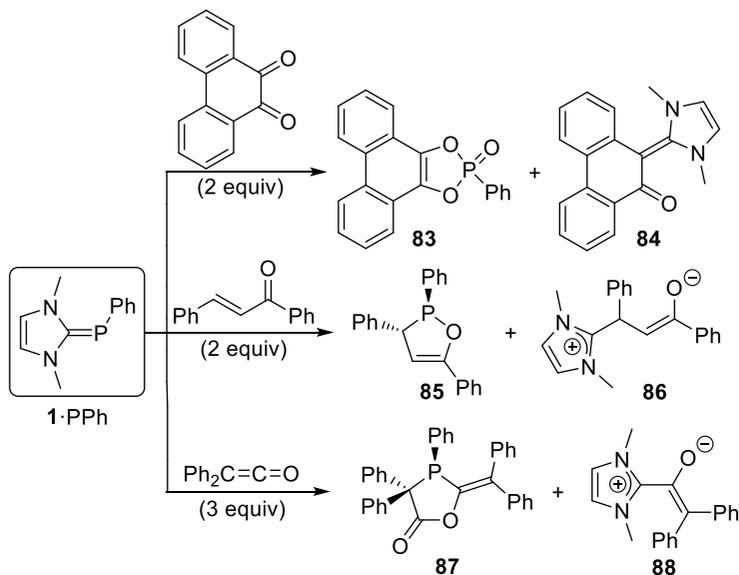
The first example of transfer of a phosphorus moiety from the NHC-stabilized molecules described in this review was reported by Grützmacher and co-workers. Namely,  $P_3$  radical **38** (Scheme 35) undergoes cycloaddition with dimethyl acetylenedicarboxylate with concomitant elimination of the two NHC fragments, followed by electron transfer to give the ion pair **82** (Scheme 51).<sup>[22]</sup> This  $P_3$  transfer reaction indicates that NHCs can stabilize reactive phosphorus fragments,<sup>[52]</sup> 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**.

Weber and co-workers demonstrated that the acyclic carbene-phosphinidene adducts  $(Me_2N)_2C=PR$  ( $R = tBu, Cy, 1-Ad, Ph, Mes$ ) can transfer the  $[PR]$  moiety to diphenylketene.<sup>[53]</sup> 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

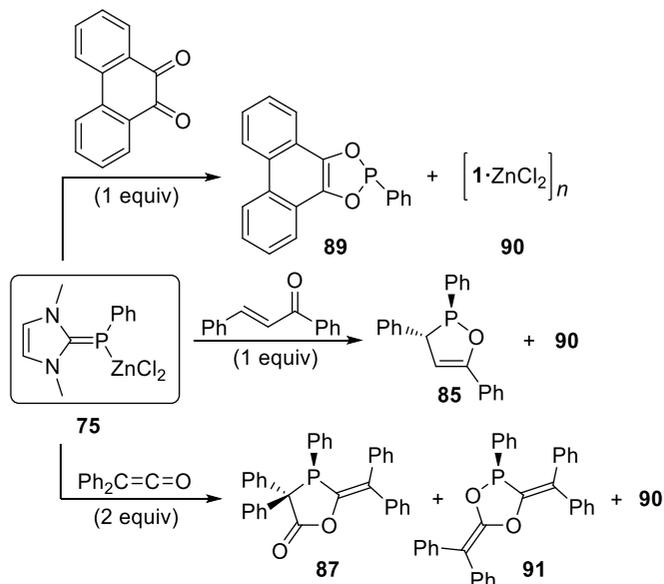
be a suitable substrate for phosphinidene transfer. Its reaction with **1**·PPh resulted in the formation of 1,3-oxaphospholan-5-one **87** as the sole phosphorus-containing product, while an additional equivalent of ketene was consumed to trap the liberated carbene **1** to afford adduct **88** (Scheme 52).<sup>[9]</sup>



**Scheme 52.** Reactivity of **1**·PPh towards *ortho*-quinone, *trans*-chalcone and diphenylketene.

Arduengo and co-workers discovered that the Lewis acid  $\text{BPh}_3$  is capable of liberating phenylphosphinidene from **5**·PPh, which was derived from the detection of the cyclopolyphosphines  $(\text{PPh})_3$ ,  $(\text{PPh})_4$  and  $(\text{PPh})_5$  in the reaction mixture (Scheme 27).<sup>[44]</sup> Similarly, Slootweg, Grützmacher *et al.* showed that treatment of **1**·PPh with  $\text{BPh}_3$ ,  $\text{AlCl}_3$ ,  $\text{MgCl}_2$  or  $\text{Zn}(\text{OAc})_2$  leads to phenylphosphinidene extrusion and the formation of the oligomeric phosphinidenes  $(\text{PPh})_n$  ( $n = 3-5$ ).<sup>[9]</sup> Selective transfer of the extruded phosphinidene to suitable substrates is possible when  $\text{ZnCl}_2$  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,  $\text{ZnCl}_2$  captured the liberated carbene to form the insoluble one-dimensional coordination polymer  $[\text{1}\cdot\text{ZnCl}_2]_n$  **90** (Scheme 53).<sup>[9]</sup>



**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  $\text{NHC}=\text{PR}$  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<sub>3</sub> 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  $\text{NHC}=\text{PR}$  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.

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