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NHC–Phosphinidene Adducts

N-Heterocyclic Carbene–Phosphinidene Adducts: Synthesis, Properties, and Applications

Tetiana Krachko^[a] and J. Chris Slootweg*^[a]

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 com-

pounds 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.

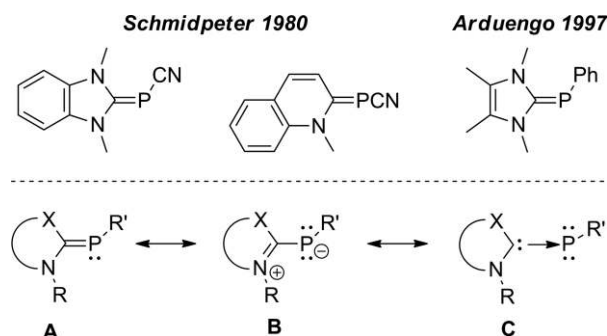
1. Introduction

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

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Carbene–phosphinidene adducts (NHC=PR) can be regarded as inversely polarized phosphalkenes^[7] and are represented by the three canonical forms **A–C** (Scheme 1). Resonance form **A** features a formal P=C double bond, **B** a zwitterion with a



Scheme 1. The first reported examples by Schmidpeter and Arduengo et al. (top) and canonical forms of NHC–phosphinidene adducts, X = CR₂, NR or S (bottom).



Tetiana Krachko was born in Berdiansk, Ukraine, in 1989, and she obtained her M.Sc. in chemistry at the Taras Shevchenko National University in Kyiv as well as at University Paul Sabatier in Toulouse in 2013. Subsequently, she pursued her doctoral studies on organophosphorus chemistry at the Van 't Hoff Institute for Molecular Sciences of the University of Amsterdam under the supervision of Assoc. Prof. Chris Slootweg. She is now working as a postdoctoral fellow in the group of Prof. Joost Reek at the same institute.



Chris Slootweg was born in Haarlem, the Netherlands, in 1978 and received his undergraduate education at Vrije Universiteit Amsterdam in 2001. After earning his Ph.D in 2005, he pursued postdoctoral studies at the ETH Zürich. In 2006, he returned to VU to initiate his independent career. He was promoted to Associate Professor in 2014 and moved to the University of Amsterdam in 2016. The mission of his laboratory is to educate students at the intersection of fundamental physical organic chemistry, main group chemistry, and circular chemistry.

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.

Table 1. ³¹P, ¹³C NMR chemical shifts (P=C_{NHC}) (recorded in C₆D₆ unless stated otherwise) and selected structural data for the adducts **1**·PR–**22**·PR.

Compound	Name	$\delta^{31}\text{P}$, ppm	$\delta^{13}\text{C}$, ppm	C _{NHC} =P bond, Å	C–P–R angle, °	Torsion angle N–C–P–R, °
	1 ·PH ^[8]	–149.3	176.0	1.763(3)	96.0(15)	0.9(18)
	1 ·PPh ^[9]	–49.1	170.1	1.7917(14) [1.7911(15)] ^[a]	101.30(6) [99.98(7)] ^[a]	48.01(16) [50.42(15)] ^[a]
	1 ·PMes ^[10]	–73.8	169.9	1.768(4)	104.6(2)	32.5(4)
	2 ·PH ^[8]	–148.8	174.7 ^[b]	1.7721(14) [1.7739(18)] ^[a]	95.9(8) [96.2(15)] ^[a]	0.2(8) [1.6(16)] ^[a]
	(2-H) ·PCHN(iPr) ₂ ^[11]	–64.8 ^[c]	178.9 ^[c]	–	–	–
	2 ·PPh ^[3]	–53.5 ^[b]	169.1 ^[b]	1.794(3)	102.34(14)	51.0(3)
	2 ·PMes ^[12]	–75.1	–	–	–	–
	2 ·P(Dmp) ^[13]	–76.7	–	1.786(4)	99.10(17)	55.5(4)
	2 ·P(EMind) ^[14]	–70.5	168.3	–	–	–
	2 ·P(Eind) ^[14]	–63.9	168.6	1.767(3)	102.72(12)	3.4(3)
	3 ·PH ^[8]	–149.9 ^[b]	173.7 ^[b]	–	–	–
	3 ·PPh ^[15,16]	–61.2 ¹⁵ –60.0 ¹⁶	167.8 ¹⁵ 168.2 ¹⁶	–	–	–
	3 ·P(pTol) ^[16]	–57.0 ^[c]	–	–	–	–
	3 ·P(DAP) ^[17]	–68.2 P ¹ (177.3 P ²)	166.8	–	–	–

Table 1. (Continued.)

Compound	Name	δ^{P} , ppm	δ^{C} , ppm	C _{NHC} =P bond, Å	C–P–R angle, °	Torsion angle N–C–P–R, °
	4-P(Dmp) ^[13]	–75.0	171.3	1.799(3)	101.53(11)	57.1(2)
	5-PH ^[8,18]	–147 ¹⁸ –147.3 ⁸	- 180.0 ^[b]	1.747(3) 1.747(2)	100(2) 101(2)	5(2) 3(2)
	5-PCF ₃ ^[19]	–23.6	168.1	1.784(2)	101.66(8)	31.3(2)
	5-PPh ^[19]	–23.0	170.0 ^[b]	1.763(6)	99.9(3)	26.5(7)
	5-PMes ^[12]	–59.1	-	1.769(3)	104.90(11)	8.3(3)
	5-PGePh ₃ ^[20]	–155.2 ^[d]	168.7 ^[d]	-	-	-
	5-PSnPh ₃ ^[20]	–179.5 ^[d]	169.4 ^[d]	1.778(3)	111.51(9)	7.1(3)
	6-PH ^[21,22,23]	–134.3 ²¹ –136.7 ²² –133.8 ²³	180.5 ²¹ 180.2 ²² 180.9 ²³	- 1.752(1) ²² 1.7509(15) ²³	- 94.5(7) 94.9(12)	- 1.2(6) 1.4(10)
	6-PPh ^[15,24]	–18.9 ¹⁵ –19.4 ²⁴	172.9 ¹⁵ -	- 1.7658(10) ²⁴	- 104.61(4)	- 24.5
	6-PMes ^[12]	–52.1	-	1.766(2)	105.74(11)	13.8(2)
	6-PSiMe ₃ ^[23]	–129.5	175.2	1.7744(13)	110.71(4)	41.01(14)
	6-PGePh ₃ ^[20]	–145.1	174.4	1.7748(16)	110.07(5)	46.89(16)
	6-PSnPh ₃ ^[20]	–161.5	174.8	1.774(3)	110.99(9)	26.2(3)
	6-PPClPh ^[25]	–17.3 P ¹ (157.6 P ²) ^[b]	169.9 ^[b]	1.8017(18)	96.35(6)	44.18(18)
	6-PPClNMe ₂ ^[25]	–33.5 P ¹ (214.1 P ²) ^[b]	170.7 ^[b]	-	-	-

Table 1. (Continued.)

Compound	Name	$\delta^{31}\text{P}$, ppm	$\delta^{13}\text{C}$, ppm	$\text{C}_{\text{NHC}}=\text{P}$ bond, Å	C–P–R angle, °	Torsion angle N–C–P–R, °
	6-PPCINiPr₂ ^[25]	–18.4 P ¹ (215.1 P ²) ^[b]	171.6	1.7835(16)	97.14(5)	36.63(19)
	Li-6-PH ^[26]	–143.0	-	1.763(2)	102	0
	7-PH ^[27]	–134.5 ^[e]	177.3 ^[e]	1.755(4)	97(2)	3(3)
	8-PCN ^[4]	–133	-	1.771(5)	101.8(5)	-
	9-PPh ^[15]	–34.6	177.4	-	-	-
	9-P(DAP) ^[17]	–35.5 P ¹ (166.3 P ²)	177.1	-	-	-
	10-PH ^[28]	–127.2	191.0 ^[b]	1.7464(16)	99.3(14)	3.4(14)
	10-PPh ^[19]	–12.0 ^[b] –10.4	184.3 ^[b]	1.746(4)	100.5(2)	19.5(5)
	11-PH ^[29]	–116.7 ^[b]	195.1	1.743(2)	104.2(17)	1.8(16)
	11-PPh ^[15]	–10.2 ^[e]	186.9 ^[e]	-	-	-
	11-PGePh₃ ^[20]	–114.7 ^[d]	192.5 ^[d]	-	-	-
	11-PSnPh₃ ^[20]	–124.6	193.1	-	-	-
	12-PPh ^[30]	78.6	169.9	1.691(4)	106.65(17)	0.77
	13-PPh ^[15,30]	39.7 ¹⁵ 37.7 ³⁰	180.3 ¹⁵ 180.1 ^[e]	-	-	-

Table 1. (Continued.)

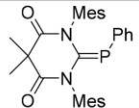
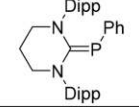
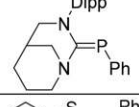
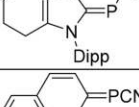
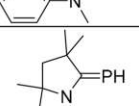
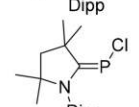
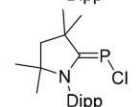
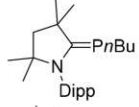
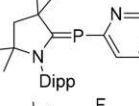
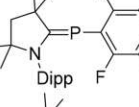
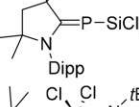
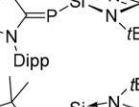
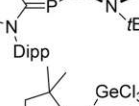
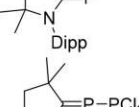
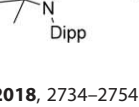

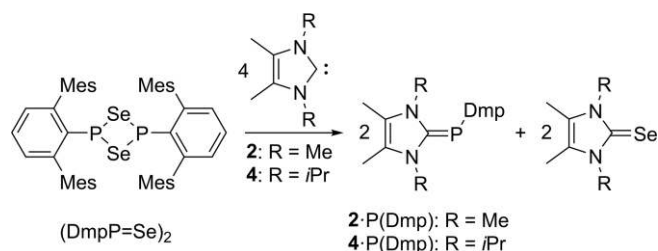
Compound	Name	$\delta^{31}\text{P}$, ppm	$\delta^{13}\text{C}$, ppm	$\text{C}_{\text{NHC}}=\text{P}$ bond, Å	$\text{C}-\text{P}-\text{R}$ angle, °	Torsion angle $\text{N}-\text{C}-\text{P}-\text{R}$, °
	14 ·PPh ^[30]	83.0	172.0 ^[e]	1.726(3)	108.22(13)	9.83
	15 ·PPh ^[15]	14.8	186.5	-	-	-
	16 ·PPh ^[15]	34.9	199.9	-	-	-
	17 ·PPh ^[15]	57.0	192.0	-	-	-
	18 ·PCN ^[4]	-38	-	-	-	-
	(E/Z)19 ·PH ^[31]	-38.3 -44.9	212.3 217.2	-	-	-
	E-19 ·PCl (94.5 %) ^[31]	161.9	210.9	1.7354(11)	103.64(4)	179.74(7)
	Z-19 ·PCl (5.5 %) ^[31]	129.4	-	1.686(6) ^[f]	96.3(3)	19.7(7)
	19 ·PnBu ^[32]	61.2	206.3	-	-	-
	19 ·P(o-Py) ^[32]	65.4	209.5	-	-	-
	19 ·P(p-C ₅ F ₄ N) ^[32]	-4.3	208.2	-	-	-
	19 ·PSiCl ₃ ^[32]	-22.0 ^[b]	217.4 ^[b]	-	-	-
	19 ·P(SiCl ₂ L) ^[33]	59.0	213.4	1.732(2)	116.43(7)	169.36(12)
	19 ·P(SiL) ^[33]	68.8	216.8	1.7303(17) [1.7381(18)] ^[a]	108.93(6) [107.05(6)] ^[a]	177.96(12) [175.83(11)] ^[a]
	19 ·PGeCl ₃ ^[32]	47.8 ^[b]	219.6	1.7653(12)	107.74(4)	161.66(8)
	19 ·PPCl ₂ ^[32]	73.9 (242.5) ^[b]	215.3	-	-	-

Table 1. (Continued.)

Compound	Name	$\delta^{31}\text{P}$, ppm	$\delta^{13}\text{C}$, ppm	C _{NHC} =P bond, Å	C–P–R angle, °	Torsion angle N–C–P–R, °
	19-PPCI(Cy) ^[32]	53.5 (135.8)	217.4	-	-	-
	19-PPPh₂ ^[32]	41.2 (-27.3)	214.3	-	-	-
	E-20-PCI (96.3 %) ^[51]	160.3	208.2	1.7404(12)	104.05(4)	178.52(7)
	Z-20-PCI (3.7 %) ^[51]	131.1	-	1.434(12) ^[f]	98.3(7)	4.7(12)
	20-P(DAP) ^[17]	76.3 P ¹ (156.6 P ²)	219.4	-	-	-
	E-21-PCI (86.3 %) ^[51]	163.4	210.1	1.7513(15)	104.51(5)	178.68(10)
	Z-21-PCI (13.7 %) ^[51]	135.0	-	1.615(4) ^[f]	98.0(2)	6.8(5)
	21-PPh ^[15]	68.9	208.1	1.7336(15)	104.94(6)	179.02(11)
	21-P(TMP) ^[34]	135.4	207.3	1.7376(14)	108.90(6)	177.00
	21-P(N=SIPr) ^[35]	134.0	199.2	1.719(2)	102.78(9)	177.30(15)
	22-PPh ^[15]	56.2	191.3	1.743(8), [1.738(8), 1.737(8), 1.723(8)] ^[a]	116.6(4), [115.2(4), 116.0(4), 115.7(4)] ^[a]	13.3(10), [4.2(9), 8.0(11), 4.0(10)] ^[a]

[a] Values for the other independent molecules are shown in square brackets. [b] The NMR spectrum was recorded in [D₈]THF. [c] The NMR spectrum was recorded in [D₈]toluene. [d] The NMR spectrum was recorded in CD₂Cl₂. [e] The NMR spectrum was recorded in CDCl₃. [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 = benzamidinate, TMP = 2,2,6,6-tetramethylpiperidine, SIPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene.

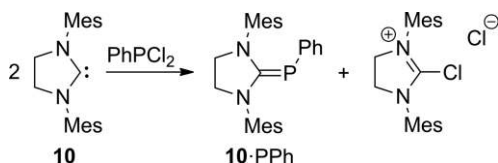
(DmpP=Se)₂ works equally well as phosphinidene synthon and yields **2**·P(Dmp).



Scheme 5. Synthesis of carbene–phosphinidene adducts using the phosphinidene selenide dimer (DmpP=Se)₂. Dmp = 2,6-dimesitylphenyl.

2.3. Chlorophosphines

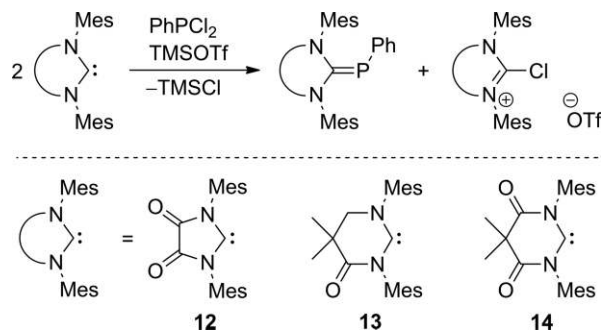
NHC=PR adducts can also be prepared from carbenes and dichlorophosphines. Arduengo et al. showed that 2 equiv. of 1,3-dimesitylimidazolin-2-ylidene (**10**) react with dichlorophenylphosphine to afford **10**·PPh ($\delta^{31}\text{P} = -10.4$) in 69 % isolated yield after removal of the 2-chloro-1,3-dimesitylimidazolium chloride byproduct by filtration (Scheme 6).^[19] The phosphorus chemical shift of **10**·PPh is about 10 ppm downfield compared to **5**·PPh which contains the analogous unsaturated NHC, however their solid-state structures are rather similar [**5**·PPh: P–C_{NHC} 1.763(6) Å, N–C–P–R 26.5(7)°; **10**·PPh: P–C_{NHC} 1.746(4) Å, N–C–P–R 19.5(5)°; see Table 1, section 3.3 and Scheme 26].



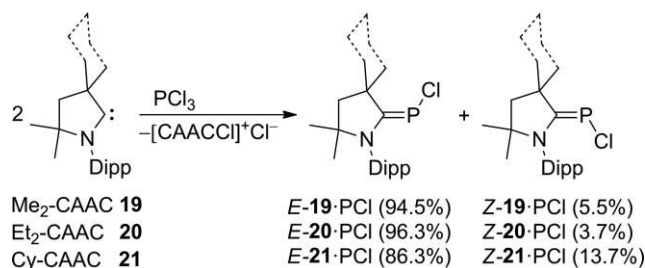
Scheme 6. Preparation of carbene–phosphinidene adduct **10**·Ph by carbene addition to phenyldichlorophosphine.

Hudnall et al. modified Arduengo's protocol to accommodate π -accepting carbonyl-decorated carbenes. They showed that treatment of PhPCl₂ 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_{NHC} 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_{NHC} 1.726(3) Å, N–C–P–R 9.83°) along with their 2-chloroiminium triflate salts in modest yields (31.9–55.4 %) (Scheme 7).^[30] Due to the increased π -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.

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

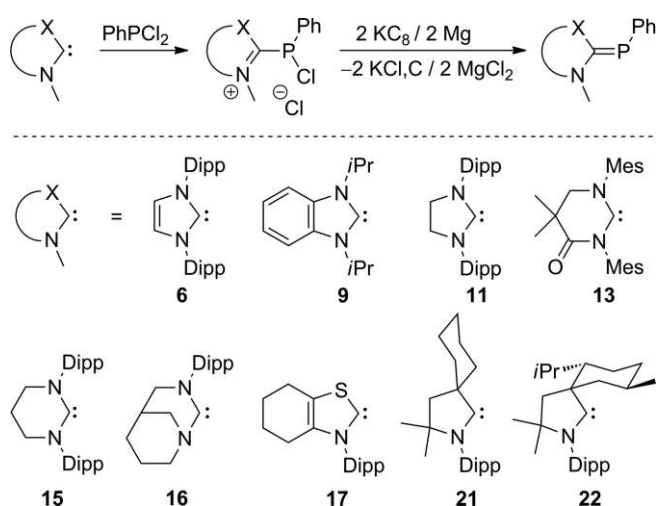


Scheme 7. Synthesis of carbonyl-decorated carbene–phosphinidene adducts from carbenes and PhPCl₂ in the presence of trimethylsilyl triflate (TMSOTf).



Scheme 8. Synthesis of CAAC–chlorophosphinidene adducts.

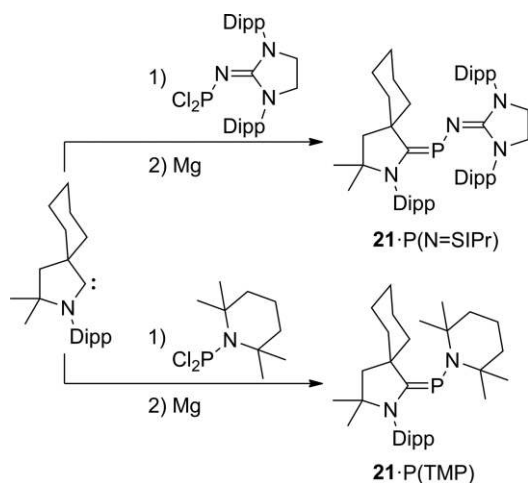
Bertrand and co-workers reported a general two-step procedure for making NHC=PR adducts from dichlorophosphines that requires only 1 equiv. of carbene. Namely, treatment of a large variety of carbenes with one equivalent of dichlorophenylphosphine results in the formation of the corresponding salts that,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



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

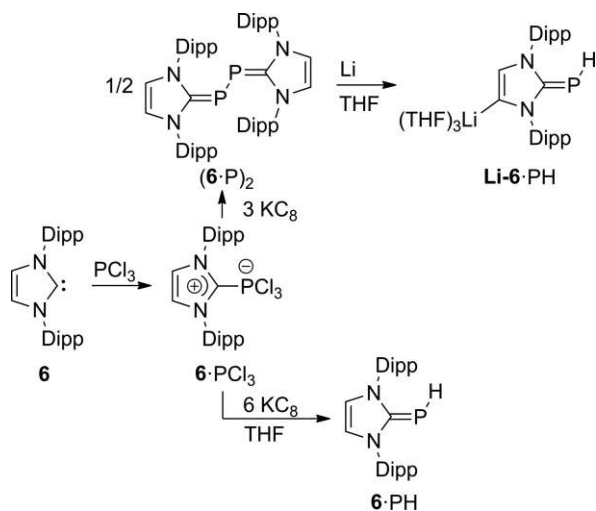
In a similar fashion cyclic (alkyl)(amino)carbene–phosphinidene adducts **21**·P(N=iPr) ($\delta^{31}\text{P} = 134.0$)^[35] and **21**·P(TMP) ($\delta^{31}\text{P} = 135.4$)^[34] have been obtained (Scheme 10), which were

subsequently used to generate phosphorus centered radical cations (see 4.1 and Scheme 31).



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

Furthermore, Robinson and co-workers have demonstrated that the reaction of PCl_3 with N-heterocyclic carbene **6** leads to adduct $\mathbf{6}\cdot\text{PCl}_3$, which upon reduction with three equivalents of potassium graphite yields carbene-stabilized diphosphorus $(\mathbf{6}\cdot\text{P})_2$ (56.6 %; $\delta^{31}\text{P} = -52.4$),^[36] and further reduction with Li metal afforded the anionic NHC-parent phosphinidene adduct $\text{Li}\cdot\mathbf{6}\cdot\text{PH}$ (16.3 %; $\delta^{31}\text{P} = -143.0$; Scheme 11).^[26] However, reduction of $\mathbf{6}\cdot\text{PCl}_3$ with six equivalents of potassium graphite afforded the neutral $\mathbf{6}\cdot\text{PH}$ in 20 % isolated yield ($\delta^{31}\text{P} = -133.9$; Scheme 11), as reported by Tamm et al.^[23]

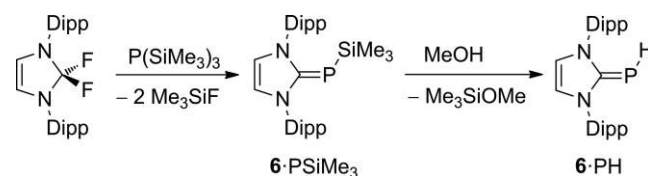


Scheme 11. Synthesis of carbene-phosphinidene adducts using PCl_3 .

2.4. Phosphines

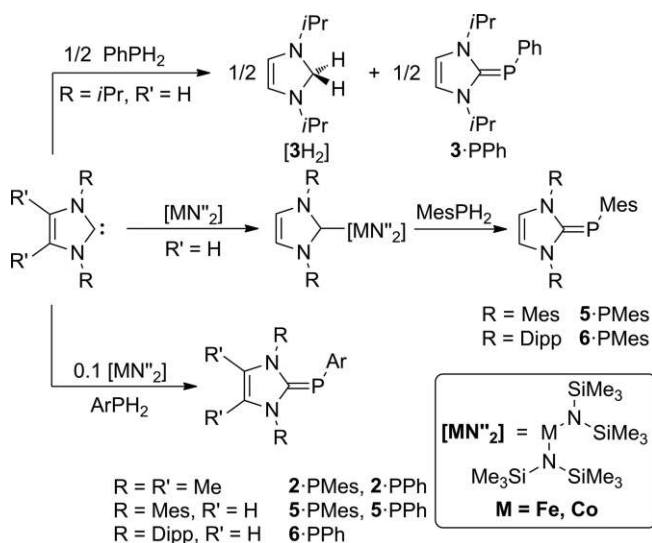
Tamm et al. described the use of tris(trimethylsilyl)phosphine as phosphorus source to access carbene-phosphinidene adducts. Treatment of *N,N'*-1,3-bis(2,6-diisopropylphenyl)-2,2-difluoroimidazoline ("PhenoFluor") with $\text{P}(\text{SiMe}_3)_3$ gives silylphosphin-

idene 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 4.4 and Scheme 49).^[23]



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

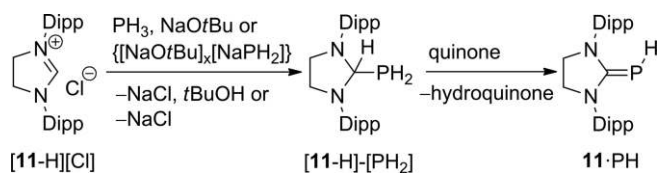
Primary phosphines follow a similar reaction course as the corresponding dichlorophosphines. Radius and co-workers showed that the reaction of one equivalent of phenylphosphine with two equivalents of 1,3-diisopropylimidazol-2-ylidene (**3**) leads to carbene-phosphinidene adduct $\mathbf{3}\cdot\text{PPh}$ ($\delta^{31}\text{P} = -60.0$) after 5 h at 105 °C in a quantitative yield next to the $[\mathbf{3H}_2]$ by-product (Scheme 13).^[16] 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}P NMR spectroscopy. The NHC acts as a phosphine activator and hydrogen acceptor in these reactions.



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

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).^[12] 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.

Phosphine gas (PH_3) can be employed to generate the corresponding NHC parent phosphinidene adducts. Grützmacher, Pringle and co-workers showed that in situ generated 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (**11**) inserts into the P–H bond of PH_3 , giving access to phosphanylimidazolidine [**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).^[29]

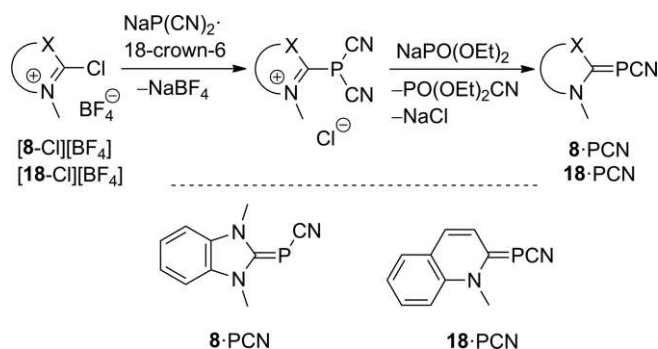


Scheme 14. Synthesis of carbene–phosphinidene adduct **11**·PH from imidazolium salt and PH_3 or $\{[\text{NaOtBu}]_x[\text{NaPH}_2]\}$ ($x \approx 2.5$). Quinone = 9,10-phenanthrenequinone.

2.5. Phosphides

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

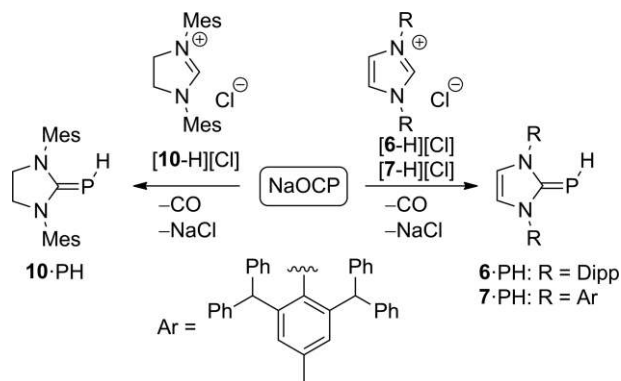
Interestingly, the first reported synthesis of N-heterocyclic carbene–phosphinidene adducts was also achieved using phosphides. In 1980, Schmidpeter and co-workers showed that carbene–cyanophosphinidene adducts **8**·PCN ($\delta^{31}\text{P} = -133$) and **18**·PCN ($\delta^{31}\text{P} = -38$) can be obtained by reacting [**8-Cl**][BF_4] and [**18-Cl**][BF_4] with [18]crown-6-sodium dicyanophosphide followed by reduction with sodium diethylphosphite (Scheme 15).^[4] The X-ray crystal structure of **8**·PCN shows a central P–C bond of 1.771(5) Å and that the two moieties (PCN and N-heterocycle) are not coplanar, which indicates a weak $\text{P}_{\text{d}t}\text{-C}_{\text{d}t}$ 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, $\text{Na}(\text{OCP})$, as a phosphorus atom

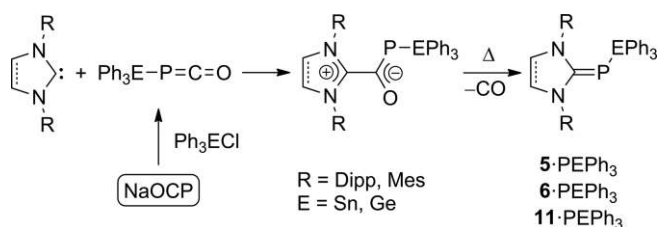
transfer reagent. Treatment of the N-arylated imidazolium salt [**6-H**][Cl] with $\text{Na}(\text{OCP})$ for 4 hours in refluxing THF afforded after work-up **6**·PH ($\delta^{31}\text{P} = -136.7$) in 71 % yield (Scheme 16).^[22] Analogously, the parent phosphinidene adducts **7**·PH (87 %; $\delta^{31}\text{P} = -134.5$)^[27] and **10**·PH (34.5 %; $\delta^{31}\text{P} = -127.2$)^[28] were prepared (Scheme 16), yet this method does not tolerate N-alkylated imidazolium salts, such as [**1-H**][Cl] and [**3-H**][Cl].^[37]



Scheme 16. Synthesis of carbene–phosphinidene adducts by phosphide transfer reactions from $\text{Na}(\text{OCP})$.

2.6. Phosphaketenes

For the synthesis of substituted phosphinidene adducts, $\text{Na}(\text{OCP})$ can also be used to prepare tetrel substituted phosphaketenes, such as $\text{Ph}_3\text{Sn}(\text{PCO})$ and $\text{Ph}_3\text{Ge}(\text{PCO})$.^[38] 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_3 ($\text{E} = \text{Sn}, \text{Ge}$) almost quantitatively (Scheme 17).^[20]



Scheme 17. Carbene–phosphinidene adduct synthesis from NHC–phosphaketene adducts.

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 (phosphanyl)phosphinidene [**P(DAP)**], by photolysis of the corresponding (phosphanyl)phosphaketene [**OCP(DAP)**] (Scheme 18).^[39] Its isolation opened a novel avenue towards NHC–phosphinidene adducts, simply by phosphinidene addition to carbenes. In this fashion, the phosphinidene

have a higher double-bond character than **19**-P(SiL), **19**-P(SiCl₂L),^[33] **6**-PH^[21] and *E*-**19**-PCl^[31] (WBI of the P–C bond are 1.57, 1.55, 1.36 and 1.535, respectively).

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 ³¹P NMR chemical shifts (between $\delta^{31}\text{P} = -179.5$ ppm for **5**-PSnPh₃^[20] and $\delta = 163.4$ ppm for *E*-**21**-PCl;^[31] see Table 1), compared to those of classical phosphaaalkenes ($\delta^{31}\text{P} = 230$ – 420 ppm).^[42] For NHC=PR adducts, Bertrand and co-workers showed that the ³¹P NMR chemical shifts can be used as indicator to evaluate the relative π -accepting properties of carbenes:^[15] more π -accepting carbenes induce stronger π -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 ³¹P NMR chemical shift more downfield. For example, the increased π -accepting capability of the saturated NHCs (**10** and **11**) compared to their unsaturated analogues (**5** and **6**) is reflected in more downfield ³¹P NMR shifts for **10**-PPh and **11**-PPh (-10.4 and -10.2 ppm) vs. **5**-PPh and **6**-PPh (-23.0 and -18.9 ppm), which corresponds with the theoretical studies discussed in 3.1.

¹H and ¹³C 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 ¹H and ¹³C NMR spectra at room temperature indicating facile rotation around the PC bond, while **11**-PPh bearing the more π -accepting saturated NHC displays broad signals caused by a hampered rotation around the more pronounced P=C bond. VT NMR studies confirm the difference in enthalpy of activation for the rotation process, namely $\Delta G^\ddagger = 34$ kJ mol⁻¹ for **6**-PPh and $\Delta G^\ddagger = 58$ kJ mol⁻¹ for **11**-PPh.^[15] Furthermore, the (**12**–**14**)-PPh adducts bearing the strongly π -accepting carbonyl-decorated carbenes **12**–**14** exhibit more downfield ³¹P 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 ¹H and ¹³C NMR spectra in solution at room temperature.^[30]

The nature of the phosphorus substituent on the NHC=PR adducts also has a significant influence on the ³¹P chemical shift. As predicted by DFT calculations,^[41c] electron-withdrawing substituents (e.g., Ph, Mes) result in more downfield ³¹P NMR shifts, whereas electron-donating groups (e.g., SiMe₃, GePh₃, SnPh₃) lead to more upfield shifts. Indeed, the ³¹P NMR chemical shifts of **6**-PPh ($\delta = -18.9$ ppm) and **6**-PMes ($\delta = -52.1$ ppm) are more downfield than the corresponding **6**-PH ($\delta = -134.3$ ppm), while adducts with electron-donating groups, like **6**-PGePh₃ ($\delta = -145.1$ ppm) and **6**-PSnPh₃ ($\delta = -161.5$ ppm), have more upfield shifts. This is in agreement with decreasing

electron-withdrawing ability in the series Ph > Mes > H > GePh₃ > SnPh₃.

Another important factor influencing the ³¹P NMR chemical shift is the stereochemistry around the P=C bond. For amino-substituted phosphaaalkenes (phosphaaamidenes) it was found that the *E*-isomers display more downfield ³¹P NMR chemical shifts than the *Z*-isomers.^[43,7a] This also holds true for the NHC=PR adducts, where the ³¹P NMR shift of the *E*-configured adduct **21**-PPh is more downfield ($\delta = 68.9$ ppm) than the signal of the related adduct **22**-PPh ($\delta = 56.2$ ppm) with a *Z*-configuration.^[15] 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 ($\delta^{31}\text{P} = 160.3$ – 163.4 ppm) than the corresponding *Z*-isomers ($\delta^{31}\text{P} = 129.4$ – 135.0 ppm).^[31]

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

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 length, 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 phosphaaalkenes (1.65–1.67 Å) and vary between 1.691(4) Å for **12**-PPh and 1.799(3) Å for **4**-P(Dmp). As expected, greater π -acidity of the carbene (e.g., **12**) leads to a shorter P–C bond, while weakly π -accepting carbenes (e.g., **4**) display elongated P–C bonds. Moreover, the degree of PC double bond character also impacts the C–P–R bond angle. In case of reduced π -back donation, the substituent on phosphorus can freely twist out of the carbene plane [e.g. **5**-PPh, N–C–P–C(Ph) 26.5(7)°, without impacting the valence angle at P [99.9(3)°] which remains similar to the that of parent phosphinidene adduct [**5**-PH, 100(2)°]. In contrast, adduct **12**-PPh that bears the same N (Mes) and P (Ph) substituents, but a more π -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

	← Increasing carbene π -acidity			
$\delta^{31}\text{P}$		78.6	-10.4	-23.0
C–P bond, Å		1.691(4)	1.746(4)	1.763(6)
C–P–C angle, °		106.65(17)	100.5(2)	99.9(3)
N–C–P–C angle, °		0.77	19.5(5)	26.5(7)

Scheme 26. Influence of carbene π -acidity on the ³¹P NMR chemical shift and selected structural parameters of NHC–phosphinidene adducts with the same P substituent.

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).

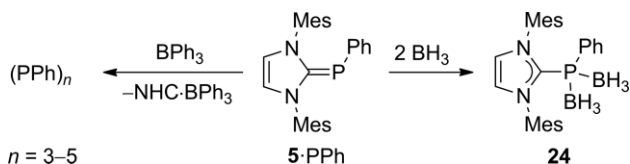
4. Reactivity of N-Heterocyclic Carbene–Phosphinidene Adducts

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.

4.1. Addition Reactions with Main-Group and Organic Compounds

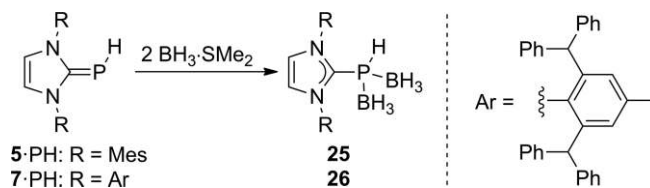
Reactions with Group 13 Electrophiles

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.^[44] Interestingly, the more sterically demanding Lewis acid BPh_3 induces formation of cyclopolymers $(\text{PPh})_n$, ($n = 3-5$; Scheme 27), which precludes the possibility of developing phosphinidene transfer reactions (see 4.5). The BH_3 groups could be removed with 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) and 1,5-diazabicyclo[4,3,0]non-5-ene (DBN) in a competition experiment, but not with the less basic phosphine PAR_3 [Ar = $\text{C}_6\text{H}_2(\text{OMe})_3-2,4,6$]. Arduengo et al. also probed for the first time the redox chemistry of NHC=PR adducts by means of cyclic voltammetry and established that **5**·PPh undergoes facile one-electron oxidation at -0.08 V (vs. SCE).



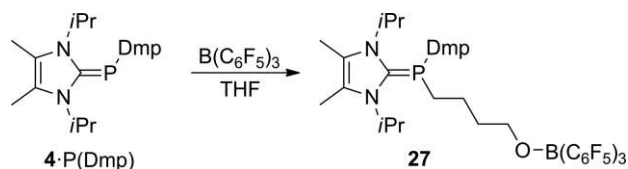
Scheme 27. Reactions of **5**·PPh with BH_3 and BPh_3 .

Following a similar protocol, the groups of von Hänisch, Bertrand, and Hahn showed that, respectively, **5**·PH,^[18] **7**·PH,^[27] and **(2-H)**·PCHN(*i*Pr)₂^[11] 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).



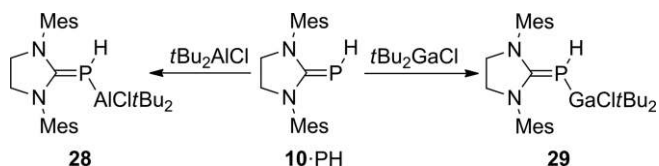
Scheme 28. Reactions of **5**·PH and **7**·PH with BH_3 .

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).^[13]



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).^[28] 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].^[28]

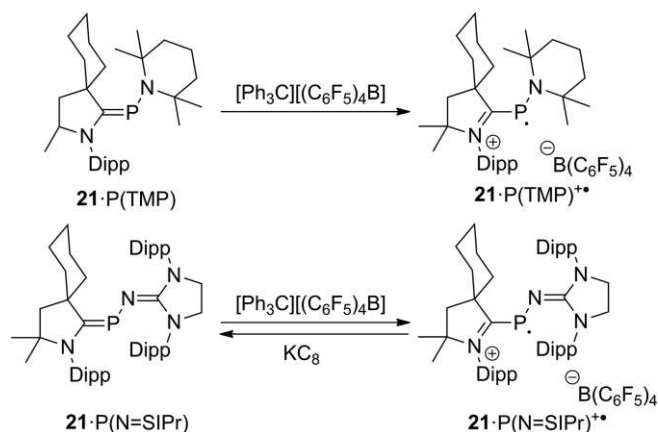


Scheme 30. Reactions of **10**·PH with $t\text{Bu}_2\text{AlCl}$ and $t\text{Bu}_2\text{GaCl}$.

Oxidation

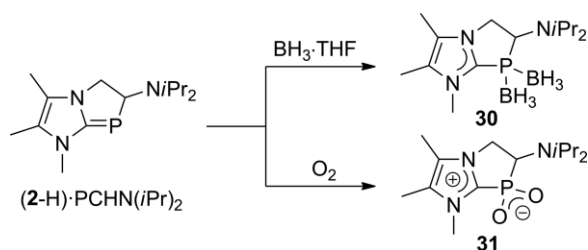
Stimulated by Arduengo's earlier results, Bertrand and co-workers investigated the redox chemistry of CAAC–phosphinidene adducts **21**·P(TMP)^[34] and **21**·P(N=SiPr)^[35] with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, which resulted in one-electron oxidation affording the thermally stable radical cations **21**·P(TMP)⁺ and **21**·P(N=SiPr)⁺ that display significant spin density on the phosphorus atom (0.67e and 0.40e, respectively), as determined by DFT calculations. Addition of KC_8 to a toluene solution of **21**·P(N=SiPr)⁺ resulted in reformation of the neutral **21**·P(N=SiPr) by one-electron reduction, thus illustrating a fully reversible redox system (Scheme 31).^[35]

Hahn and co-workers applied oxygen from air as oxidant serendipitously. Namely, upon exposure of NHC–phosphinidene adduct **(2-H)**·PCHN(*i*Pr)₂ ($\delta^{31}\text{P} = -64.8$) in benzene to air for several weeks a small amount of bis(oxide) **31** ($\delta^{31}\text{P} = 90.5$) was obtained and crystallographically characterized (Scheme 32).^[11] Recently, the group of Tamm has demonstrated that **2**·PPh,



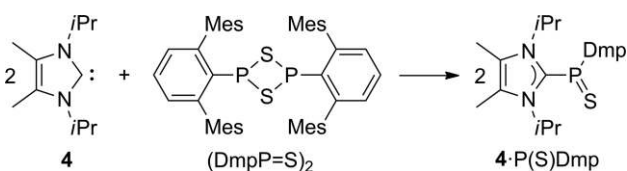
Scheme 31. Redox chemistry of CAAC-phosphenidene adducts.

5·PPh and **6**·PPh can also form the corresponding bis(oxides) in the reaction with dioxygen, whereas the heavier sulfur and selenium analogues are selectively obtained only in the reaction of the sterically accessible **2**·PPh with elemental sulfur or selenium, respectively.^[45]



Scheme 32. Reactions of (2-H)·PCHN(iPr)₂ with BH₃ 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 (DmpP=S)₂ ($\delta^{31}\text{P} = 124$) with two equivalents of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**4**) at room temperature to afford the first monomeric phosphenidene sulfide **4**·P(S)Dmp ($\delta^{31}\text{P} = 29$; Scheme 33).^[46]

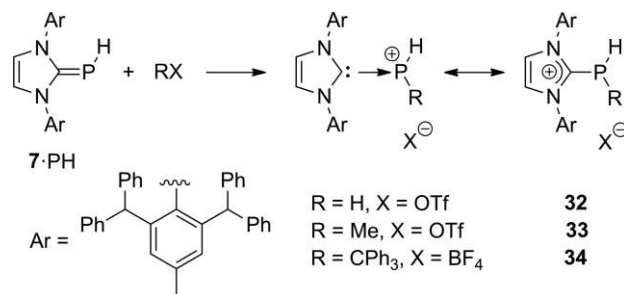


Scheme 33. Synthesis of a NHC-stabilized phosphenidene sulfide.

Protonation and Alkylation

Next to neutral Lewis acids and oxidants, the reactivity of NHC=PR adducts has also been studied towards cationic electrophiles. Bertrand and co-workers have demonstrated that the sterically encumbered parent phosphenidene adduct **7**·PH can be protonated and alkylated at the phosphorus atom. Addition of trifluoromethanesulfonic acid (HOTf) to a benzene solution

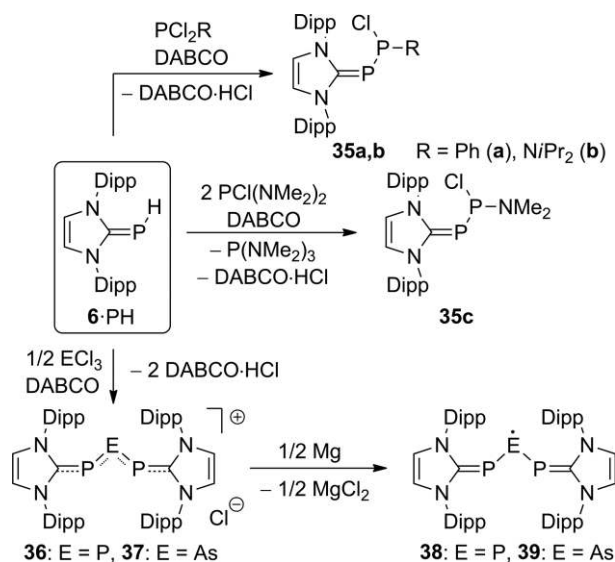
of **7**·PH ($\delta^{31}\text{P} = -134.5$) afforded the NHC-stabilized parent phosphonium salt **32** (85 %, $\delta^{31}\text{P} = -166.6$; Scheme 34), while alkylation was achieved by treatment of **7**·PH with methyl trifluoromethanesulfonate (MeOTf) and [Ph₃C][BF₄] resulting in NHC-stabilized phosphonium salts **33** (87 %, $\delta^{31}\text{P} = -86.3$) and **34** (89 %, $\delta^{31}\text{P} = -49.4$), respectively (Scheme 34).^[27]



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

4.2. Substitution Reactions with Main-Group and Organic Compounds

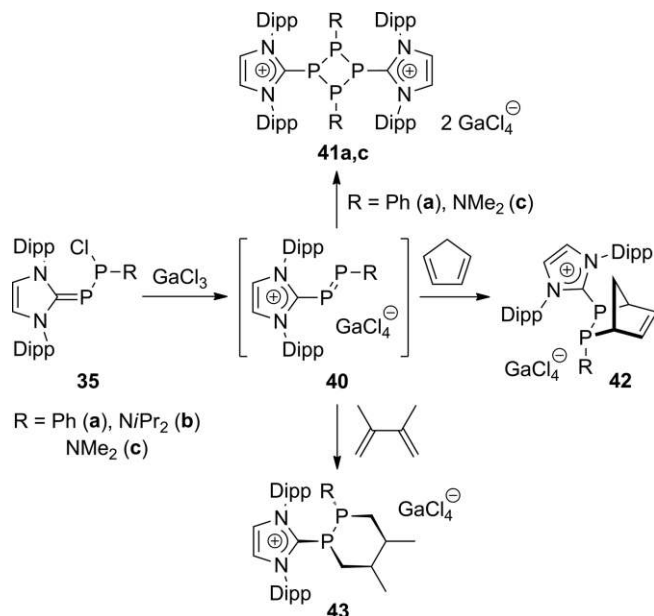
Apart from functioning as a strong Lewis base (see 4.1), PH- and PCI-functionalized N-heterocyclic carbene phosphenidene adducts can also undergo substitution reactions at the phosphorus center offering an alternative approach to create functionalized NHC=PR adducts. For example, Grützmacher and co-workers showed that the parent phosphenidene-carbene adduct **6**·PH ($\delta^{31}\text{P} = -136.7$) reacts with dichlorophosphines PCI₂R in the presence of the non-nucleophilic base DABCO (1,4-diazabicyclo[2.2.2]octane) to yield the neutral species **6**·PPCIR **35** [R = Ph (**a**; $\delta^{31}\text{P} = -17.3$) or NiPr₂ (**b**; $\delta^{31}\text{P} = -18.4$; see Scheme 35)].^[25] However, treatment of **6**·PH with chlorobis(dimethylamino)phosphine does not afford **6**·PP(NMe₂)₂, but **6**·PPCINMe₂ **35c** ($\delta^{31}\text{P} = -33.5$) and P(NMe₂)₃ as a second equivalent of PCI(NMe₂)₂ acts as chloride donor (Scheme 35).^[25] The



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

pnictogen chlorides 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 P_3 and PAsP cations **36** [$\delta^{31}\text{P} = 190.6$ ($\text{P}=\text{C}$), 591.9], **37** ($\delta^{31}\text{P} = 218.9$) (Scheme 35).^[22] Further reactions of **36** and **37** with magnesium metal led to the reduction of both compounds into the neutral radicals **38** and **39**. Moreover, phosphorus radical **38** was able to undergo a [3+2] cycloaddition to formally result in P_3 transfer (see 4.5 and Scheme 51).^[22]

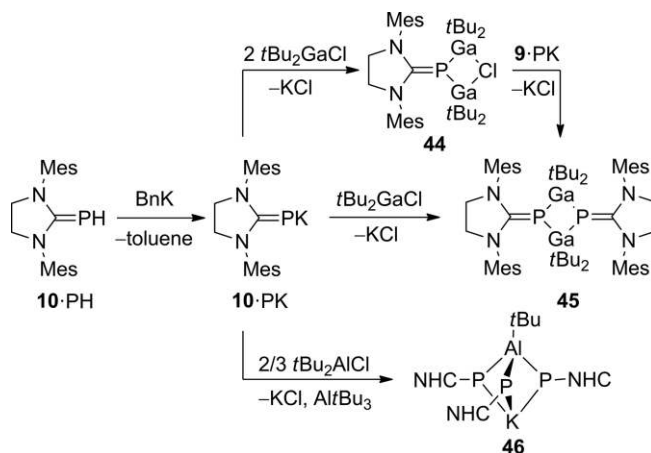
Chlorophosphines **35** offer interesting follow-up chemistry. Namely, treatment of **35** with gallium trichloride resulted in chloride abstraction and the formation of the corresponding cationic diphosphenes $[\text{6}\cdot\text{P}=\text{PR}]^+ \text{40}$, which depending on the steric bulk of the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



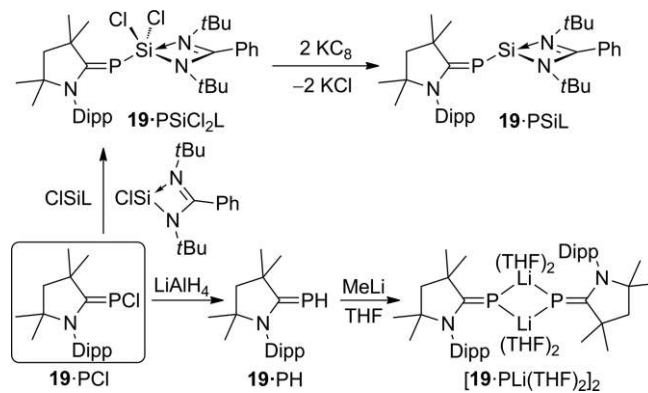
Scheme 36. Chloride abstraction reactions of **35** with GaCl_3 both in the presence and absence of trapping agents.

The group of von Hänisch and collaborators demonstrated that the saturated NHC phosphinidene adduct **10-PH** can be deprotonated using benzyl potassium resulting in NHC–phosphinidene **10-PK**, which can be functionalized with $t\text{Bu}_2\text{MCl}$ ($\text{M} = \text{Al}, \text{Ga}$) affording aluminium and gallium phosphinidene complexes **44–46** (Scheme 37).^[28]

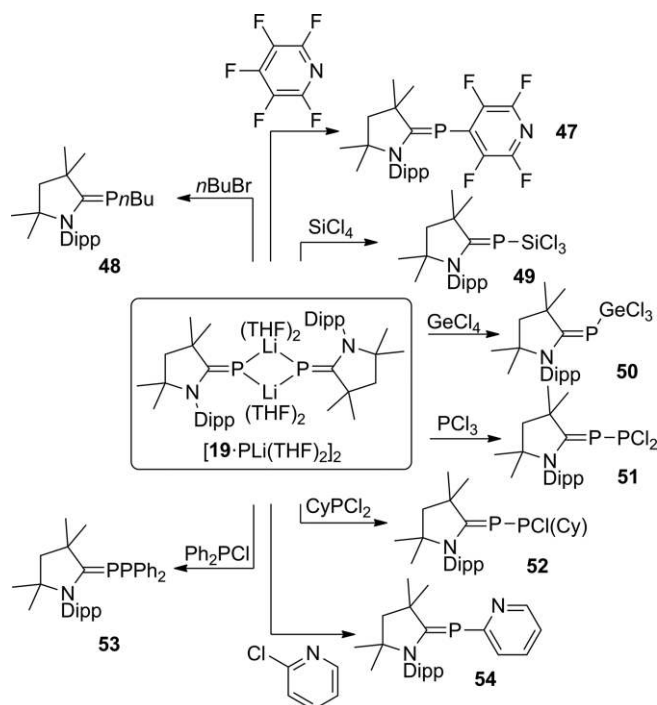
Frenking, Stalke, Roesky, and co-workers have reported on the functionalization of chlorophosphinidene adduct **19-PCl** ($\delta^{31}\text{P} = 161.9/129.4$), which oxidatively adds to chlorosilylene LSiCl ($\text{L} = \text{benzamidinate}$) affording dichlorosilane **19-PSiCl₂L** (84 %, $\delta^{31}\text{P} = 59.0$) 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).^[33] Reduction of chlorophosphinidene adduct **19-PCl** with LiAlH_4 affords the parent phosphinidene–CAAC adduct **19-PH** (70 %, $\delta^{31}\text{P} = 161.9/129.4$), which can be further functionalized with MeLi in THF to form the lithium phosphinidene complex **[19-PLi(THF)₂]₂** (Scheme 39).



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



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



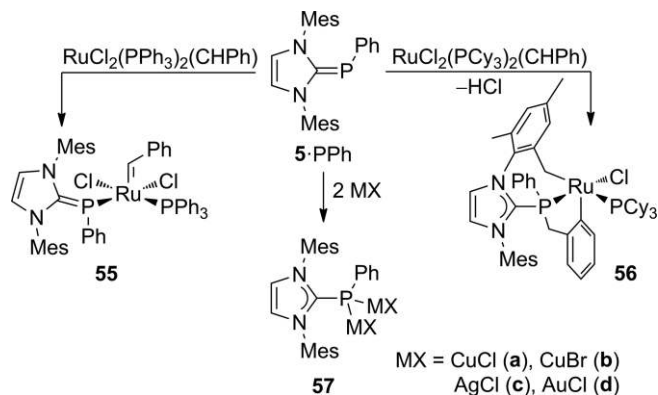
Scheme 39. Reactions of base-stabilized phosphorus atom with organic and inorganic substrates. Cy = cyclohexyl.

$\delta^{31}\text{P} = -38.4/-44.9$),^[31] which upon lithiation with MeLi in THF gives lithium phosphinidene [19•PLi(THF)₂]₂ (65 %, $\delta^{31}\text{P} = 177.3$; Scheme 38).^[32]

Lithium phosphinidene [19•PLi(THF)₂]₂ can be considered as a monoanionic phosphorus atom stabilized by CAAC and was used as a precursor for the synthesis of various base-stabilized phosphinidenes containing P–C [19•P(*p*-C₆F₄N) (**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•PSiCl₃ (**49**; 67 %, $\delta^{31}\text{P} = -22.0$)], P–Ge [19•PGeCl₃ (**50**; 85 %, $\delta^{31}\text{P} = 47.8$)] and P–P bonds [19•PPCl₂ (**51**; 76 %, $\delta^{31}\text{P} = 242.5, 73.9$), 19•PPCl(Cy) (**52**; 75 %, $\delta^{31}\text{P} = 135.8, 53.5$), 19•PPPh₂ (**53**; 80 %, $\delta^{31}\text{P} = 41.2, -27.3$; see Scheme 39)].^[32]

4.3. Addition Reactions with Transition-Metal Complexes

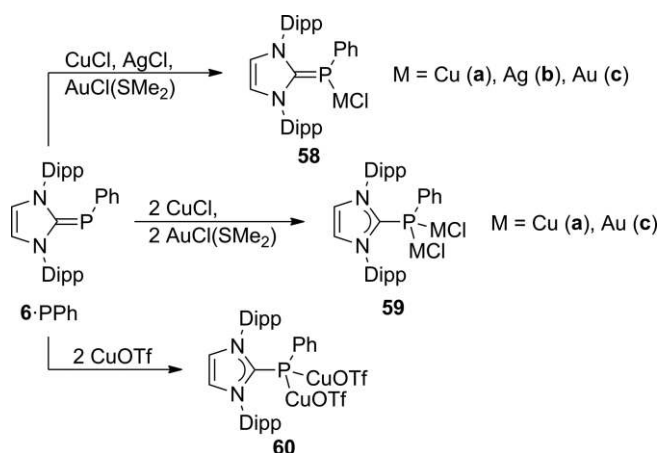
N-Heterocyclic carbene–phosphinidene adducts have been treated with a variety of transition-metal complexes leading to, in analogy to the main-group based Lewis acids, η^1 -coordination to either one or both of the available lone pairs at the phosphorus site (see 4.1). The first study exploring the coordination 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.^[47] Addition of 5•PPh (1 equiv.) to RuCl₂(PPh₃)₂(CHPh) (CHPh) resulted in ligand exchange and the formation of η^1 -coordination product **55**, which was, however, inactive in ring-opening metathesis of diallyl sulfide. The use of RuCl₂(PCy₃)₂(CHPh) did not afford RuCl₂(5•PPh)(PCy₃)(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.

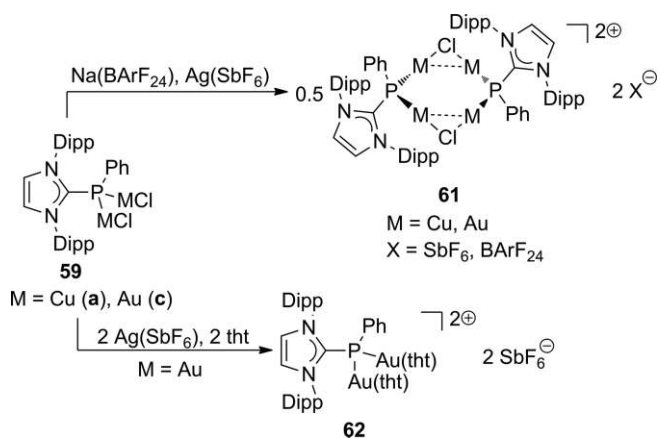
Dias and co-workers explored the coordination chemistry of 5•PPh towards coinage metals and prepared the bimetallic coinage metal complexes **57** (Scheme 40).^[48] While copper(I) and silver(I) adducts **57a–c** crystallized as halide ion bridged octanuclear complexes, bis-gold(I) chloride adduct **57d** 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).^[24] Depending on the stoichiometry of the reactions with CuCl and AuCl(SMe₂), monometallic **58a,c** or bimetallic complexes **59a,c** were iso-

lated, 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 (vs. 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.

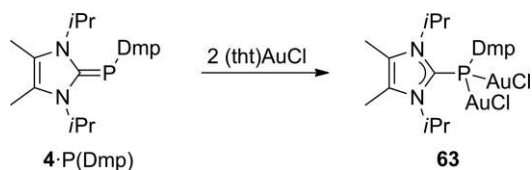
Subsequent treatment of the bimetallic complexes **59** (M = Cu, Au) with chloride abstraction reagents (NaBARF₂₄ or AgSbF₆) gave the dicationic tetranuclear complexes **61**, which feature a remarkable central eight-membered ring bearing short Cu...Cu and Au...Au distances, respectively, along the chlorine-bridged metal–metal axes (Scheme 42).^[24] Complete chloride abstraction was observed by reacting **59c** with two equivalents of AgSbF₆ in the presence of tetrahydrothiophene (tth), 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. tth = tetrahydrothiophene.

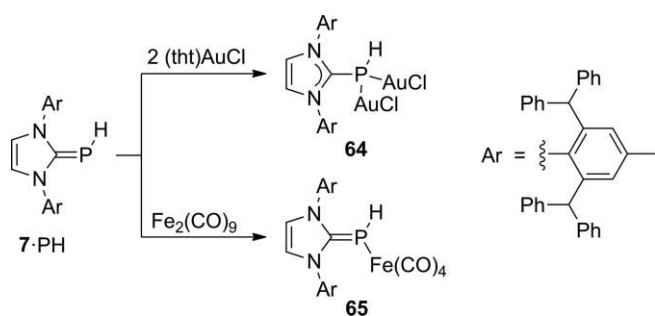
Ragogna and co-workers explored the coordination of (tth)AuCl to 4•P(Dmp) ($\delta^{31}\text{P} = -75.0$). This reaction resulted in

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.^[13]



Scheme 43. Reaction of 4-P(Dmp) with (tetrahydrothiophene)gold(I) chloride. Dmp = 2,6-dimesitylphenyl, tht = tetrahydrothiophene.

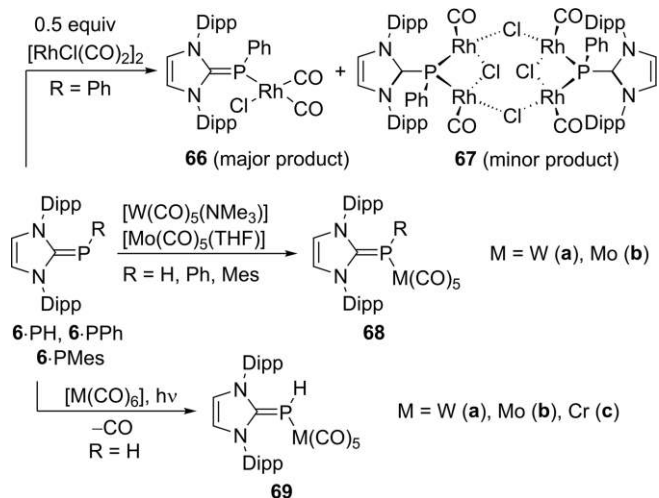
Bertrand and co-workers have demonstrated that also the parent carbene–phosphinidene adduct **7-PH** reacts with two equivalents of (tht)AuCl resulting in bis-metal complex **64** (Scheme 44).^[27] In contrast, treatment of **7-PH** with diiron nonacarbonyl led to mono-iron complex **65**, due to steric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



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

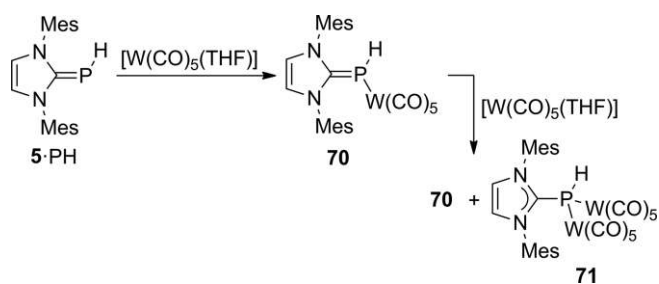
To probe the P-donor properties of the NHC=PR adducts, Tamm and co-workers reacted **6-PR** (R = H, Ph, Mes) with the metal carbonyl complexes $[\text{Rh}(\mu\text{-Cl})(\text{CO})_2]_2$, $[\text{W}(\text{CO})_5(\text{NMe}_3)]$ and $[\text{Mo}(\text{CO})_5(\text{THF})]$ to afford dicarbonyl rhodium(I) complex **66**, tetranuclear complex **67**, and tungsten and molybdenum pentacarbonyl complexes **68** (M = Mo, W), respectively (Scheme 45).^[49] IR spectroscopic analysis of the CO stretching frequencies of **66** and **68** revealed the much stronger electron-donating ability of the carbene–phosphinidene adducts **6-PR**, when compared to phosphines and NHCs. Values similar to those of the related carbodicarbenes, also bearing two lone pairs on the donor atom, were observed.^[50]

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).^[37] 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



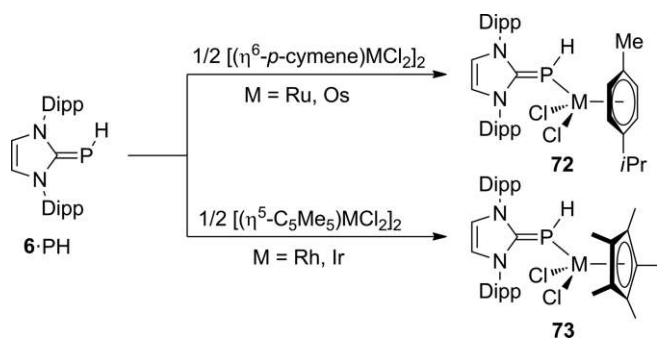
Scheme 45. Synthesis of transition metal carbonyl complexes of carbene–phosphinidene adducts **6-PH**, **6-PPh** and **6-PMes**.

(Scheme 46).^[18] Interestingly, these carbonyl complexes mimic carbene adducts of the transient electrophilic phosphinidenes $[\text{R}=\text{M}(\text{CO})_5]$, such as $[\{\mathbf{2}\text{-PR}\}\text{W}(\text{CO})_5]$ [R = $\text{CH}(\text{SiMe}_3)_2$] that was prepared by Streubel and co-workers.^[51]



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

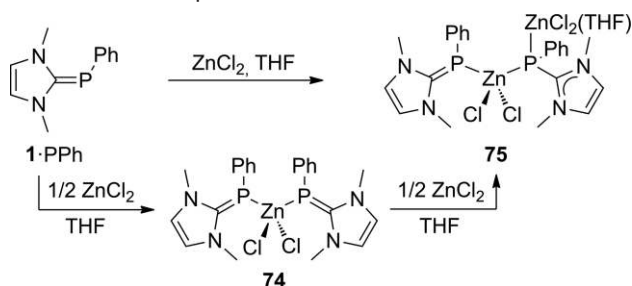
The reactivity of carbene–phosphinidene adduct **6-PH** towards group 8 and 9 metal complexes has been investigated by Tamm and co-workers (Scheme 47). Addition of dimeric complexes of the type $[\text{LMCl}_2]_2$ (M = Ru, Os, Rh, Ir) to **6-PH** afforded the three-legged piano-stool complexes $[\{\mathbf{6}\text{-PH}\}\text{M}(\text{L})\text{Cl}_2]$ **72** (M = Ru/Os, L = η^6 -*p*-cymene) and **73** (M = Rh/Ir, L = η^5 - C_5Me_5), which upon dehydrochlorination with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) can partly be converted



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

into the corresponding NHC–phosphinidene complexes **76** and **77** (see 4.4 and Scheme 49).^[52]

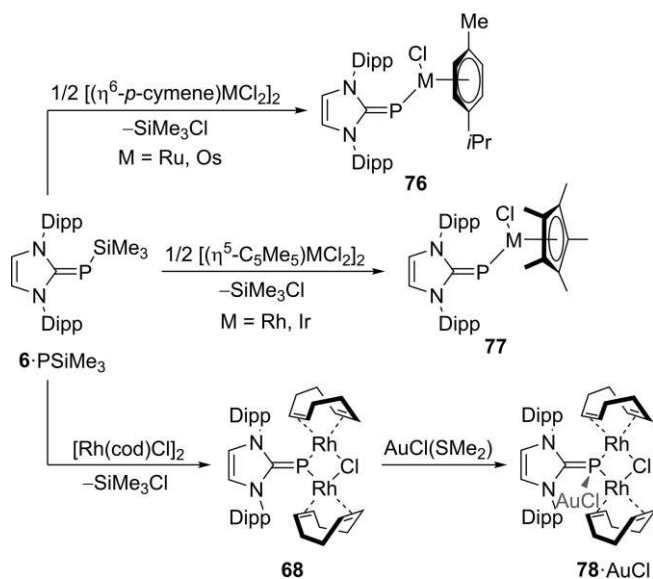
Slootweg, Grützmacher and co-workers explored the reactivity of carbene–phosphinidene adduct **1**·PPh towards ZnCl₂ (Scheme 48). Namely, reaction of **1**·PPh with half an equivalent of ZnCl₂ led to bis(**1**·PPh) zinc complex **74**, which upon addition of another half equivalent of ZnCl₂ afforded the 1:1 zinc carbene–phosphinidene complex **75**.^[9] The latter can also be obtained directly by treating **1**·PPh with one equivalent of ZnCl₂. Interestingly, ZnCl₂ complexation of NHC–phosphinidene adduct **1**·PPh induced selective phenylphosphinidene transfer reactions to electron-poor heterodienes (see 4.5 and Scheme 53).



Scheme 48. Synthesis of ZnCl₂ complexes of carbene–phosphinidene adduct **1**·PPh.

4.4. Substitution Reactions with Transition-Metal Complexes

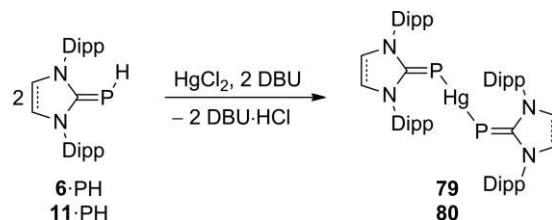
Besides complexation, NHC=PH and NHC=Psiyl adducts can undergo substitution reactions with transition-metal halides. Tamm and co-workers reacted **6**·PSiMe₃ with the dinuclear metal halides [LMCl₂]₂ (M = Ru/Os, L = η⁶-*p*-cymene; M = Rh/Ir, L = η⁵-C₅Me₅) and [Rh(cod)Cl]₂ to afford, after elimination of trimethylsilyl chloride, the NHC–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).^[23,52] Complexes **76–78** can



Scheme 49. Synthesis of carbene–phosphinidene metal complexes of ruthenium(II), osmium(II), rhodium(III), iridium(III) and rhodium(I).

be reacted further with AuCl(SMe₂) to yield bimetallic complexes **76**·AuCl, **77**·AuCl and trimetallic complex **78**·AuCl (see Scheme 49) with three- and four-coordinate phosphorus atoms, respectively.^[23]

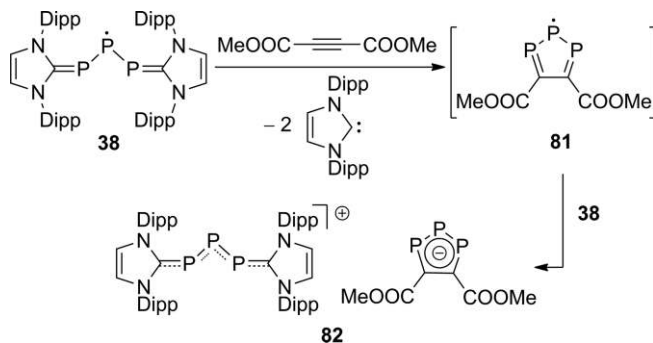
Grützmacher, Pringle and co-workers have demonstrated that the parent NHC=PHs **6**·PH and **11**·PH can be converted into the corresponding linear bis(carbene–phosphinidene) Hg complexes **79** and **80** by treatment with half an equivalent of mercury(II) chloride in the presence of DBU (Scheme 50).^[29]



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

4.5. Phosphinidene Transfer Reactions

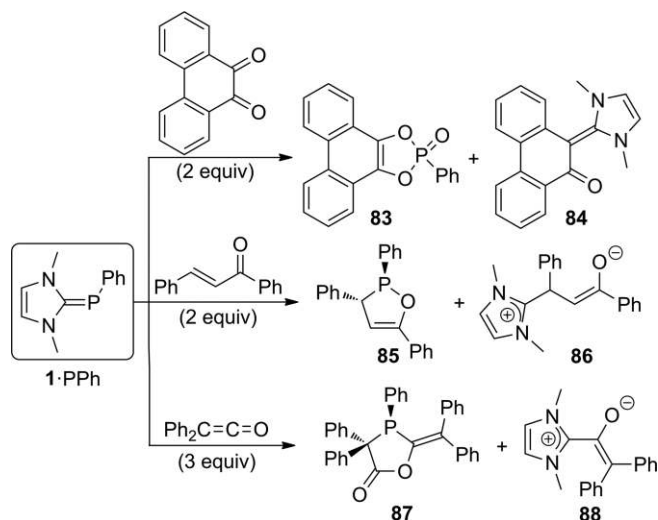
The first example of transfer of a phosphorus moiety from the NHC-stabilized molecules described in this review was reported by Grützmacher and co-workers. Namely, P₃ radical **38** (Scheme 35) undergoes cycloaddition with dimethyl acetylenedicarboxylate with concomitant elimination of the two NHC fragments, followed by electron transfer to give the ion pair **82** (Scheme 51).^[22] This P₃ transfer reaction indicates that NHCs can stabilize reactive phosphorus fragments,^[53] but also facilitate their subsequent transfer to substrate molecules, which stimulated the quest for facile phosphinidene transfer reactions from NHC=PR adducts.



Scheme 51. P₃ transfer reaction from **38** to an activated alkyne to give **82**.

Weber and co-workers demonstrated that the acyclic carbene–phosphinidene adducts (Me₂N)₂C=PR (R = *t*Bu, Cy, 1-Ad, Ph, Mes) can transfer the [PR] moiety to diphenylketene.^[54] 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*-chal-

one led to an intractable mixture of products, from which oxo-3-phospholene **85** and the zwitterionic carbene–chalcone adduct **86** could be isolated. Diphenylketene also proved in this case to be a suitable substrate for phosphinidene transfer. Its reaction with **1**·PPh resulted in the formation of 1,3-oxaphospholan-5-one **87** as the sole phosphorus-containing product, while an additional equivalent of ketene was consumed to trap the liberated carbene **1** to afford adduct **88** (Scheme 52).^[9]

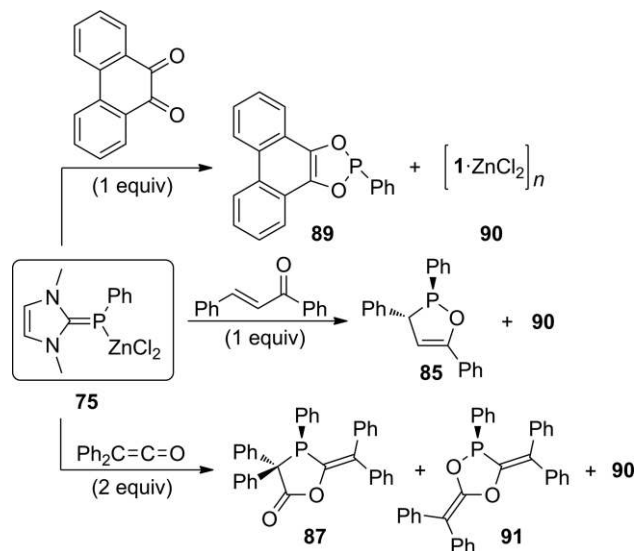


Scheme 52. Reactivity of **1**·PPh towards *ortho*-quinone, *trans*-chalcone and diphenylketene.

Arduengo and co-workers discovered that the Lewis acid BPh_3 is capable of liberating phenylphosphinidene from **5**·PPh, which was derived from the detection of the cyclopolyphosphines $(\text{PPh})_3$, $(\text{PPh})_4$ and $(\text{PPh})_5$ in the reaction mixture (Scheme 27).^[44] Similarly, Slootweg, Grützmacher et al. showed that treatment of **1**·PPh with BPh_3 , AlCl_3 , MgCl_2 or $\text{Zn}(\text{OAc})_2$ leads to phenylphosphinidene extrusion and the formation of the oligomeric phosphinidenes $(\text{PPh})_n$ ($n = 3-5$).^[9] Selective transfer of the extruded phosphinidene to suitable substrates is possible when ZnCl_2 is used as Lewis acid. Thus, zinc complex **75** allowed phenylphosphinidene transfer to form phosphonite **89** in the reaction with 9,10-phenanthrenequinone, oxo-3-phospholene **85** when applying *trans*-chalcone, and a mixture of 1,4,2-dioxaphospholane **91** and 1,3-oxaphospholan-5-one **87** while using diphenylketene as substrate. In all cases, ZnCl_2 captured the liberated carbene to form the insoluble one-dimensional coordination polymer $[\text{1} \cdot \text{ZnCl}_2]_n$ **90** (Scheme 53).^[9]

5. Summary and Conclusion

The past five years have shown an 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–SiMe₃ substituted analogues display facile substitution reactions expanding the scope of differently substituted



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

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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Keywords: Carbene ligands · Phosphinidenes · Main group elements · Adducts · Phosphinidene transfer

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