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# On 1,3-phosphaazaallenes and their diverse reactivity†

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1,3-Phosphaazaallenes are heteroallenes of the type  $RP=C=NR'$  and little is known about their reactivity. In here we describe the straightforward synthesis of  $ArPCNR$  ( $Ar = Mes^*$ , 2,4,6-*t*Bu-C<sub>6</sub>H<sub>2</sub>; <sup>Mes</sup>Ter, 2,6-(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)-C<sub>6</sub>H<sub>3</sub>; <sup>Dip</sup>Ter, 2,6-(2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>2</sub>)-C<sub>6</sub>H<sub>3</sub>; R = *t*Bu; Xyl, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) starting from phosphawittig reagents  $ArPPMe_3$  and isonitriles CNR. It is further shown that  $ArPCNtBu$  are thermally labile with respect to the loss of iso-butene and it is shown that the cyanophosphines  $ArP(H)CN$  are synthetically feasible and form the corresponding phosphanitrilium borates with  $B(C_6F_5)_3$ , whereas deprotonation of <sup>Dip</sup>TerP(H)CN was shown to give an isolable cyanidophosphide. Lastly, the reactivity of  $ArPCNR$  towards Pier's borane was investigated, showing hydroboration of the C=N bond in  $Mes^*PCNtBu$  to give a hetero-butadiene, while with <sup>Dip</sup>TerPCNXyl the formation of the Lewis acid–base adduct with a B–P linkage was observed.

## Introduction

1,3-Phosphaazaallenes ( $RP=C=NR$ ) are a heteroallene subclass. The first derivative  $tBuPCNtBu$  was obtained by combining  $tBuP(SiMe_3)C(OSiMe_3)=NtBu$  with NaOH under the release of hexamethyldisiloxane.<sup>1,2</sup> Although known for almost 40 years, 1,3-phosphaazaallenes have been scarcely investigated, especially when compared to the “lighter” carbodiimides and other heteroallene analogues. Another synthetic route was disclosed by Yoshifuji,<sup>3,4</sup> and Appel,<sup>5</sup> who reacted  $Mes^*P(Li)SiMe_2tBu$  ( $Mes^* = 2,4,6-tBu_3C_6H_2$ ) with isocyanates in a Peterson-type reaction to give  $Mes^*PCNR$  (R = Ph, *n*Pr, *t*Bu). In 2000, Zhou and co-workers expanded this series to include  $Mes^*PCN(4-ClC_6H_4)$ ,<sup>6</sup>  $Mes^*PCN(4-ClC_6H_4)$  and  $Mes^*PCNPh$ <sup>4</sup> are the only structurally characterized 1,3-phosphaazaallenes bearing classic organic substituents. Sterically demanding groups on the P atom suppress dimerization to the corresponding 1,3-diphosphetanes, which can only be reconverted to the 1,3-phosphaazaallenes by flash vacuum pyrolysis.<sup>2,7</sup> Even  $Mes^*PCNPh$  slowly dimerizes in solution, whereas in the presence of catalytic amounts of  $Pd(PPh_3)_4$  the unsymmetric four-membered heterocycle is obtained.<sup>8</sup> Derivatives with a bulky cyclopropen-1-yl substituent at the phosphorus were synthesized by Regitz *et al.*<sup>9</sup>

In 1991 Grobe and co-workers demonstrated that the metastable  $(F_3C)PCNtBu$  (can be handled at  $-40\text{ }^\circ\text{C}$ ) is feasible by reacting the phosphalkene precursor  $(F_3C)P=CF_2$  with three equivalents of  $H_2NtBu$ .<sup>10</sup> Instead of dimerizing at higher temperatures,  $(F_3C)PCNtBu$  decomposes to give fluorinated cyclophosphanes  $(PCF_3)_n$  and the isocyanide  $CNtBu$ . Stephan *et al.* showed that the zirconocene phosphinidene  $Cp_2(PMe_3)Zr=PMes^*$  reacts with an isothiocyanate in a [2 + 2] cycloaddition/cycloreversion sequence to yield  $Mes^*PCNPh$  and  $[Cp_2ZrS]_2$ .<sup>11</sup> That 1,3-phosphaazaallenes can function as ligands for transition metals was established by Streubel and Jones.<sup>12</sup> Photochemical ring opening in the presence of an isocyanide of a  $W(CO)_5$ -stabilized 2*H*-azaphosphirene resulted in the formation of an 1,3-phosphaazaallene with the P atom remaining coordinated to  $W(CO)_5$ . A transient terminal phosphinidene complex is assumed to react in a 1,1-addition with the respective isocyanide. The motif to generate 1,3-phosphaazaallenes directly in the coordination sphere of a transition metal by reactions of metal-bound phosphinidenes with isocyanides is more common in the literature.<sup>13</sup> A trimethylstannyl substitution at the phosphorus centre in 1,3-phosphaazaallenes was achieved by reacting the potassium 1,3-azaphosphaallenide  $K[iPrNCP]$  with  $ClSnMe_3$  in a salt metathesis reaction, thus revealing another access to this substance class.<sup>14</sup> The most recent examples of 1,3-phosphaazaallenes were synthesized by Bertrand *et al.* in coupling reactions of (phosphino)phosphinidenes with isocyanides.<sup>15</sup> Moreover, Scheschkewitz *et al.* showed that a phosphasilene with a mobile  $NMe_2$ -functionality on the phosphorus atom undergoes an  $NMe_2$ -shift in the reaction with  $CNtBu$  to give a P-silyl-substituted 1,3-phosphaazaallene.<sup>16</sup> The synthetic protocols towards 1,3-phosphaazaallenes are summarized in Scheme 1. Even though

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observed.<sup>29</sup> The NMR data of **3a–f** are in accordance to the previously reported data of **3a** in CDCl<sub>3</sub> (Table 1).<sup>4</sup> The <sup>31</sup>P{<sup>1</sup>H} NMR signals of **3a–3f** range from –103.9 to –145.4 ppm and are generally shifted to higher field when the N-substituent is aromatic with the P-substituent being the same. This was corroborated by DFT calculations at the PBE0-D3/def2SVP level of theory, which gave  $\delta_{\text{calc}}(^{31}\text{P})$  values that are systematically at lower ppm values, though the experimentally observed trends are followed (Table 1).

Highly characteristic for **3a–f** are the <sup>13</sup>C{<sup>1</sup>H}NMR signals of the two-coordinate carbon atoms of the PCN moieties, being significantly deshielded ( $\delta^{13}\text{C}\{^1\text{H}\} = 177.9$  to 192.2 ppm) and showing <sup>1</sup>J<sub>P,C</sub> coupling constants of 73.0 to 78.1 Hz (Table 1). Additionally, the molecular structures of **3a**, **3e**, and **3f** could be determined by single crystal X-ray diffraction (SC-XRD, Fig. 1, Table 2). The P–C bond lengths of **3a**, **3e**, and **3f** of 1.6658(15) Å (**3a**) to 1.6785(12) Å (**3f**) are slightly elongated compared to **I** (1.651 Å) and **II** (1.642(5) Å), respectively, but are shorter than the sum of the covalent double bond radii ( $\Sigma r_{\text{cov}}(\text{P}=\text{C}) = 1.69$  Å).<sup>30</sup> The N–C bond lengths of **3a**, **3e**, and **3f** (1.2009(15) Å to 1.2037(19) Å) are in the expected range for heteroallenes (*cf.* XylN=C=Nxyl d(C–N) 1.197(2), 1.206(3) Å).<sup>31,32</sup> Noteworthy, the P–C–N angles deviate from linearity (as expected for sp-hybridized carbon atoms) but are in good agreement to previously structurally characterized 1,3-phosphaazaallenes (Table 2).

The bonding in **3a–f** was studied using the truncated model compound MesPCNMe on the PBE0-D3/def2SVP level of theory. Inspection of the Kohn–Sham orbitals revealed a HOMO best described as a polarized P–C  $\pi$ -bond, while the LUMO shows major contribution from the C–N  $\pi^*$  orbital interacting with a s-type lone pair on phosphorus (Fig. 2, top). With an energetically high lying HOMO the 1,3-phosphaazaallenes might be potentially oxidized to give the corresponding radical cation, as was recently shown for vinyl-substituted diphosphenes.<sup>33</sup> CV studies on **3a** show an irreversible oxidation event at  $E_{1/2} = 0.38$  V vs. Fc/Fc<sup>+</sup> (Fig. S82–S84†), and the corresponding radical cation might be synthetically feasible. We next evaluated the NPA (Natural Population Analysis) charges indicating a minimal charge transfer from the MesP-fragment to the CNMe moiety by –0.196e, with a positive partial charge on P of 0.37e and 0.07e

on the two-coordinate C atom. Natural Bond Orbital (NBO) analysis supports the description as an heteroallene, with a LP of electrons on P and polarized  $\sigma$ - and  $\pi$ -P=CMe (WBI 1.64) and PC=NMe (WBI 2.05) double bonds, respectively. In agreement with the KS-orbitals the  $\pi$ -component is polarized towards the P atom (58.3% P, 41.7% C), whereas the  $\sigma$ -component is inversely polarized (34.5% P, 65.5% C). Analysis of the second order perturbation of the Fock matrix revealed delocalization of the lone pair of electrons (LP) on P into the CN  $\pi^*$ -orbital resulting in a stabilization energy of 12.7 kcal mol<sup>–1</sup>. Natural resonance theory analysis (NRT) revealed two leading resonance structures, with the 1,3-phosphaazaallene being the dominant form (31.7%) and an ylidic formulation with a C≡N triple bond and thus two LPs on P (14.8%) (Fig. 2, bottom).

### Formation of cyanophosphines starting from **3a–c**

When a solution of **3a** was heated to 105 °C in toluene-*d*<sub>8</sub> a new species with a <sup>31</sup>P{<sup>1</sup>H} NMR chemical shift of –105.6 ppm (*cf.* **3a**  $\delta^{31}\text{P}\{^1\text{H}\} = -103.9$  ppm) was observed along with minimal amounts of the diphosphene Mes\*P=PMes\* ( $\delta^{31}\text{P}\{^1\text{H}\} = 493.2$  ppm). This transformation is accompanied by the formation of iso-butene, as evident from two signals in the <sup>1</sup>H NMR spectrum in a 3 : 1 ratio at 1.60 (triplet) and 4.75 (heptet) ppm, respectively. Finally, the multinuclear and multidimensional NMR data clearly showed that the new compound is the cyanophosphine Mes\*P(H)CN (**4a**) (Scheme 3). Isobutene elimination and formal HCN transfer has been previously observed with disilynes,<sup>34</sup> whereas with boracumulenes and transient borylenes CN<sup>–</sup> transfer was observed, with formation of a mixture of iso-butane and -butene.<sup>35,36</sup> Streubel and co-workers showed that the  $\eta^1$ -1,3-phosphaazaallene complex (Me<sub>3</sub>Si)<sub>2</sub>HC–P(W(CO)<sub>5</sub>)CN*t*Bu undergoes thermal loss of iso-butene to give the corresponding cyanophosphine tungsten complex.<sup>12</sup> The thermodynamic feasibility of this transformation was elucidated at the PBE0-D3/def2SVP//DNLPO-CCSD(T)/def2TZVP level of theory, showing that the formation of **4a** is exergonic by –36.93 kJ mol<sup>–1</sup>, whereas the dimerization of **3a** to give Mes\*P=PMes\* and CN*t*Bu is less favored ( $\Delta_{\text{R}}G = -5.68$  kJ mol<sup>–1</sup>). A scan of the potential energy surface revealed that the H-shift from the *t*Bu-group to P occurs intramolecularly

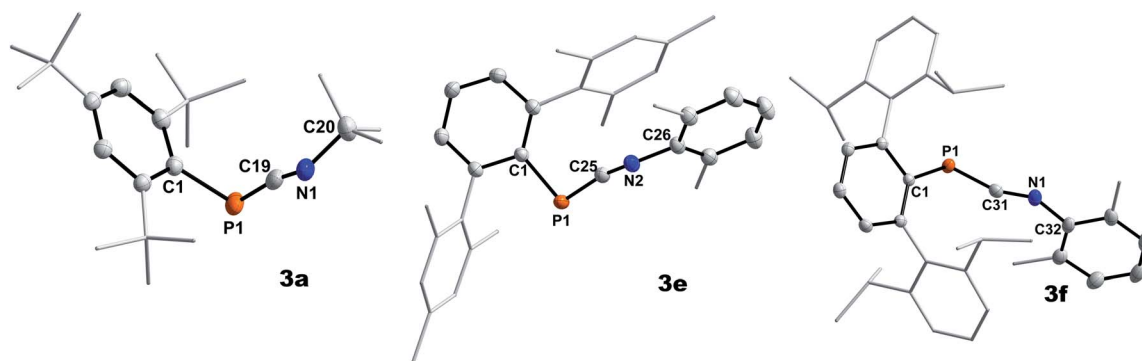


Fig. 1 Molecular structures of **3a** (left), **3e** (middle), and **3f** (right). Hydrogen omitted and parts of the molecule rendered as wireframe for clarity. Thermal ellipsoids are drawn at the 50% probability level. Structural parameters are summarized in Table 2.



Table 2 Selected bond lengths [Å] and angles [°] of **3a**, **3e** and **3f** (literature known species I and II for comparison)

Compound	P–C	N–C	P–C–N	C–P–C	C–N–C
<b>3a</b>	1.6690(15)	1.2034(18)	170.38(12)	97.92(6)	130.02(13)
<b>3e</b>	1.6658(15)	1.2037(19)	167.14(13)	103.06(7)	139.44(15)
<b>3f</b>	1.6785(12)	1.2009(15)	160.00(10)	107.53(5)	143.24(12)
Mes*PCNPh ( <b>I</b> ) <sup>4</sup>	1.651	1.209	171.1	99.2	130.5
Mes*PCN( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> ) ( <b>II</b> ) <sup>6</sup>	1.642(5)	1.214(6)	170.8(4)	99.8(2)	128.3(4)

via a six-membered transition state ( $\Delta_{\#}G = 156.1 \text{ kJ mol}^{-1}$ ), resulting in P–H bond formation as the C(sp<sup>3</sup>)–H and N–C<sub>tBu</sub> bonds are cleaved (Fig. S87<sup>†</sup>). This rather high energy barrier is in line with prolonged heating of the reaction mixture at 105 °C. An alternative radical pathway through N–C<sub>tBu</sub> bond homolysis and formation of a *t*Bu<sup>•</sup> radical was excluded as this would result in disproportionation and a mixture of iso-butene and iso-butane. The intermediate formation of free phosphinidenes is also unlikely, as this would give rise to cyclo-metalated species in case of Mes\* and <sup>Dip</sup>Ter, which were not observed by NMR spectroscopy. Alternatively, **4a** can be prepared directly in one pot starting from **1a** and **2a** (Scheme 3, bottom).<sup>16</sup> Following this route **4a** was isolated as a colourless solid in good yields of 75%. Given the PH functionality, the <sup>1</sup>H NMR spectrum shows a characteristic doublet at 5.57 ppm with a <sup>1</sup>J<sub>P,H</sub> coupling constant of 252.3 Hz, which is corroborated by the <sup>31</sup>P NMR spectrum. To further elaborate the scope of this reaction, the

analogous <sup>Mes</sup>TerP(H)CN (**4b**) and <sup>Dip</sup>TerP(H)CN (**4c**) derivatives were synthesized, and their characteristic NMR data is shown in Table 3. Surprisingly, in the IR spectrum of **4a** and **4c** no characteristic CN band is detected, in agreement with frequency analyses at the PBE0-D3/def2SVP level of theory. The presence of a P–H moiety was corroborated by a band at 2411 and 2310 cm<sup>-1</sup> for **4a** and **4c**, respectively. Cyanophosphines of the general type RP(H)CN (R = alkyl, aryl) have long remained elusive and were either found to be unstable,<sup>37</sup> or to be stabilized by coordination to a transition metal.<sup>38</sup>

In 2001 the reaction of dicyanophosphines (RP(CN)<sub>2</sub>) with equimolar amounts of Schwartz's reagent ([Cp<sub>2</sub>Zr(H)Cl]<sub>n</sub>) was shown to afford the methyl, *tert*-butyl, and Mes\* derivatives, respectively.<sup>39</sup> However, structural data of this compound class is missing in the literature and the molecular structures of **4a–c** could be determined by SC-XRD (Fig. 3, Table 4). The C–N bond lengths in **4a–c** average 1.146 Å and indicate triple bonds ( $\Sigma r_{\text{cov}}(\text{C}\equiv\text{N}) = 1.14 \text{ \AA}$ ),<sup>30</sup> in agreement with the formulation as cyanophosphines. The average P–C bond length of 1.791 Å is shorter than the respective single bond covalent radii ( $\Sigma r_{\text{cov}}(\text{P–C}) = 1.86 \text{ \AA}$ ),<sup>30</sup> with a nearly linear arrangement of the P–C–N unit (>176°). Similar bond lengths were reported for Mes\*P(CN)<sub>2</sub> (P–C<sub>avg</sub> 1.80 Å, N–C<sub>avg</sub> 1.14 Å).<sup>39</sup> NBO analyses of **4a–c** at the PBE0-D3/def2SVP//PBE0/def2SVP level of theory support the notation as cyanophosphines with CN triple bonds (WBI C≡N **4a** 2.88, **4b** 2.87, **4c** 2.87), a polar P<sup>δ+</sup>–C<sup>δ-</sup><sub>CN</sub> single bond and a LP on P, which is minimally delocalized into two π\* orbitals of the CN group with a stabilization energy of *ca.* 12 kcal mol<sup>-1</sup>.<sup>17</sup>

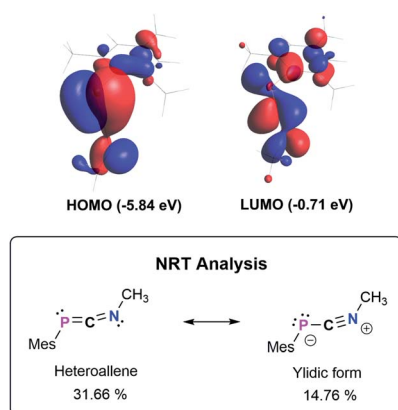
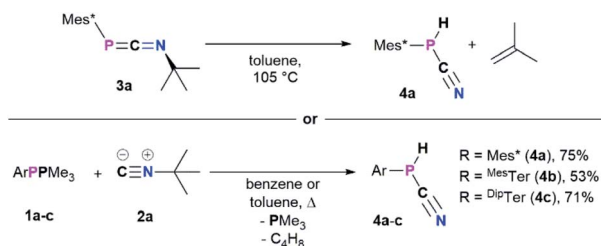


Fig. 2 Selected Kohn–Sham orbitals of the truncated model compound MesPCNMe (PBE0–D3/def2SVP) and leading resonance structures according to NRT analysis.



Scheme 3 Formation of the cyanophosphines **4a–c** from **3a–c** (top) or directly from **1a–c** and *t*BuNC (**2a**).

### Reactivity of cyanophosphines towards B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>

**4a–c** possess two potential binding sites for Lewis acids, the LPs on P and N, even though steric congestion should render the phosphorus rather inaccessible. By reacting **4a–c** with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, the first examples of the corresponding phosphanitrilium borates RP(H)CNB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (R = Mes\* (**5a**), R = <sup>Mes</sup>Ter (**5b**), R = <sup>Dip</sup>Ter (**5c**)) were prepared (Scheme 4). The reactions were performed on NMR scale and **5a** was exemplarily isolated as a colourless solid in a moderate yield of 55%. The coordination to the borane moiety results in a minimal deshielding of the PH unit accompanied by a slight increase of the <sup>1</sup>J<sub>P,H</sub> coupling constant in both the <sup>1</sup>H and <sup>31</sup>P NMR spectra ( $\delta(^1\text{H}) = 5.61 \text{ ppm}$ ,  $\delta(^{31}\text{P}) = -99.2 \text{ ppm}$ , <sup>1</sup>J<sub>P,H</sub> = 260.0 Hz;  $\delta_{\text{calc}}(^{31}\text{P}) = -140.9 \text{ ppm}$ ), respectively, when compared to the starting material **4a** ( $\delta(^1\text{H}) = 5.57 \text{ ppm}$ ,  $\delta(^{31}\text{P}) = -105.4 \text{ ppm}$ , <sup>1</sup>J<sub>P,H</sub> = 252.3 Hz). The signals of the C≡N group are unaltered (**5a**:  $\delta(^{13}\text{C}\{^1\text{H}\}) = 121.0 \text{ ppm}$ , *c.f.* **4a**:  $\delta(^{13}\text{C}\{^1\text{H}\}) = 120.8 \text{ Hz}$ ), while the <sup>1</sup>J<sub>P,C</sub> coupling constant



Table 3 Characteristic  $^{31}\text{P}\{^1\text{H}\}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR data of **4a–c**. Calculated  $^{31}\text{P}$  NMR shifts (PBE0-D3/def2SVP) are given in parentheses

Compound <sup>a</sup>	$\delta^1\text{H}$ (PH)	$\delta^{31}\text{P}$ ( $\delta_{\text{calc}}^{31}\text{P}$ )	$^1J_{\text{P,H}}$ (PH)	$\delta^{13}\text{C}$ (C≡N)	$^1J_{\text{P,C}}$ (C≡N)
<b>4a</b>	5.57 [5.95] <sup>b</sup>	−105.4 [−101.6] <sup>b</sup> (−139.1)	252.3 [249.7] <sup>b</sup>	120.8 [121.2] <sup>b</sup>	76.3 [74.4] <sup>b</sup>
<b>4b</b>	4.38	−120.6 (−154.9)	244.8	116.7	76.7
<b>4c</b>	4.35	−120.4 (−154.6)	247.2	116.6	75.3
<b>5a</b>	5.61	−99.2 ( )	260.0	121.0	106.8
<b>5b</b>	4.61	−115.1	250.9	—	—
<b>5c</b>	5.03	−108.3	256.1	—	—
MeP(H)CN <sup>39</sup>	4.15	−119.9	227.5	119.6	70.9

<sup>a</sup> In  $\text{C}_6\text{D}_6$  at room temperature; values in ppm ( $\delta$ ) or Hz ( $J$ ). <sup>b</sup> previously reported NMR data for **4a** was collected in  $\text{CD}_2\text{Cl}_2$  [values given in brackets].<sup>39</sup>

increases significantly to  $^1J_{\text{P,C}} = 106.8$  Hz (cf. **4a**  $^1J_{\text{P,C}} = 76.3$  Hz). Interestingly, in the IR spectrum the CN stretch is now visible as a weak band at  $2265\text{ cm}^{-1}$ . The  $^{11}\text{B}\{^1\text{H}\}$  NMR resonance at  $-10.3$  ppm is consistent with tetra-substituted boron atoms bearing perfluorinated aryl groups (cf. [K(18-crown-6)] [SCNB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]:  $\delta(^{11}\text{B}\{^1\text{H}\}) = -12.4$  ppm).<sup>40</sup> The three C<sub>6</sub>F<sub>5</sub> groups are equivalent as verified by the respective  $^{19}\text{F}$  NMR spectrum ( $\delta(^{19}\text{F}\{^1\text{H}\}) = -133.9$  (*meta*),  $-155.8$  (*para*), and  $-163.4$  (*ortho*) ppm;  $\Delta(\delta)^{19}\text{F}_{m,p} = 7.6$  Hz), which is in agreement with other nitrilium borates with a heteroatom at the carbon atom of the C≡N triple bond (cf. PhSCNB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>:  $\delta(^{19}\text{F}\{^1\text{H}\}) = -134.0$  (*meta*),  $-155.7$  (*para*), and  $-163.3$  (*ortho*) ppm;  $\Delta(\delta)^{19}\text{F}_{m,p} = 7.6$  Hz).<sup>41</sup> The molecular structure of **5a** (Fig. 4) confirms the four-coordinate boron atom and the BNCP axis is in a nearly linear arrangement (P1–C19–N1  $175.7(2)^\circ$ , C19–N1–B1  $178.3(2)^\circ$ ). The N1–C19 bond length of  $1.136(3)$  Å is still diagnostic of a triple bond (cf. **4a**  $1.143(4)$  Å;  $\Sigma r_{\text{cov}}(\text{C}\equiv\text{N}) = 1.14$  Å).<sup>30</sup> The newly formed N1–B1 bond ( $1.584(3)$  Å) is in the same range as reported for PhSCNB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> ( $1.5829(10)$  Å)<sup>41</sup> and slightly shorter when compared to classic nitrile–B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> adducts (cf. MeCNB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>  $1.616(3)$  Å).<sup>42</sup>

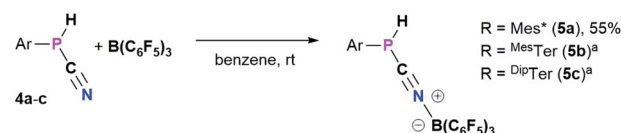
### Attempted syntheses of cyanophosphides

With **4a–c** in hand, we envisioned to synthesize the corresponding cyanophosphides [RPCN]<sup>−</sup> through simple deprotonation of **4a–c**. The first dicyanophosphides [P(CN)<sub>2</sub>]M were isolated by Schmidpeter *et al.* through reductive decyanation of P(CN)<sub>3</sub>,<sup>43</sup> and alternative synthetic strategies have surfaced since this initial report.<sup>44–46</sup> Schmidpeter and co-workers then

Table 4 Selected bond lengths [Å] and angles [°] of **4a–c** and **5a**

Compound	P–C	N–C	P–C–N	C–P–C
<b>4a</b>	1.796(3)	1.143(4)	176.4(3)	97.49(11)
<b>4b</b>	1.7853(18)	1.148(2)	177.41(16)	100.31(6)
<b>4c</b>	1.793(2)	1.146(3)	177.5(2)	99.32(9)
<b>5a</b>	1.799(3)	1.136(3)	175.7(2)	97.71(11)

synthesized [PhPCN]M (M<sup>+</sup> = Na, K, [(Ph<sub>3</sub>P)<sub>2</sub>N]) by reacting Ph<sub>3</sub>P<sub>5</sub> with the corresponding cyanides as equilibrium mixtures, which is shifted to [PhPCN]M when using weakly-coordinating cations.<sup>47–49</sup> Recently, Grützmacher *et al.* introduced alkali phosphanyl cyanophosphides [(NHP)PCN]M (NHP = N-heterocyclic phosphonium, M = Na, K) as versatile PCN building blocks, by an oxygen for nitrogen exchange from phosphanyl phosphaketenes of the general type (NHP)PCO with (M(NSiMe<sub>3</sub>)<sub>2</sub>) (M = alkali metal) and concomitant formation of O(SiMe<sub>3</sub>)<sub>2</sub>.<sup>50</sup> Wolf, Weigand and co-workers observed the formation of the phosphanyl-substituted cyanophosphides



Scheme 4 Synthesis of phosphanitriliumborates ArP(H)CNB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> **5a–c**.<sup>a</sup> NMR reactions, products were not isolated.

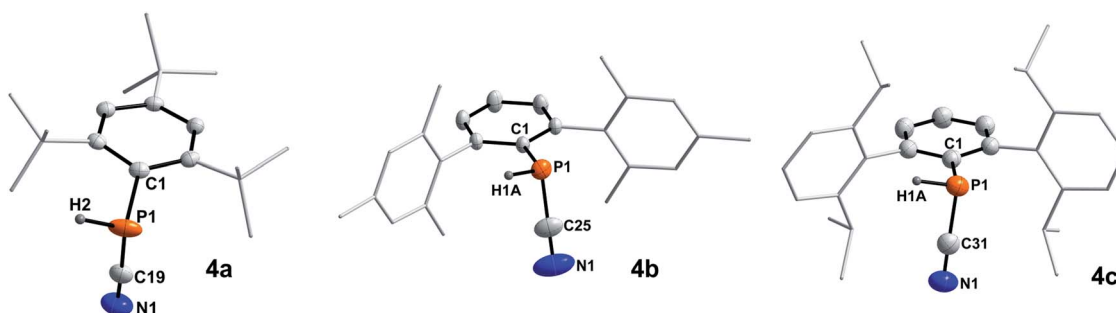


Fig. 3 Molecular structures of **4a** (left), **4b** (middle), and **4c** (right). Hydrogen atoms (except on P1) omitted and parts of the molecules rendered as wireframe for clarity. Thermal ellipsoids are drawn at the 50% probability level. Structural parameters are summarized in Table 4.



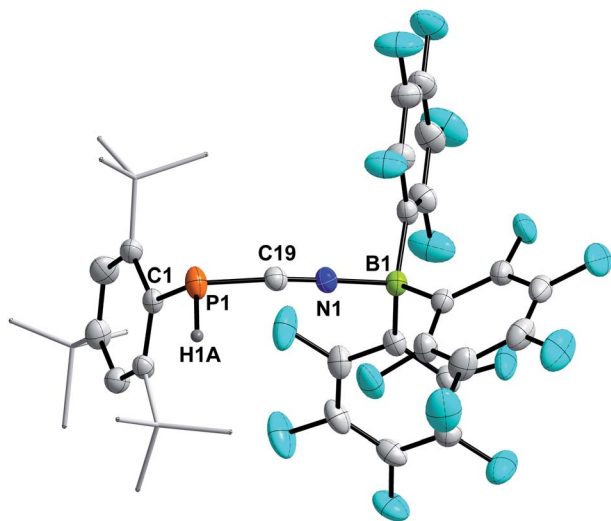


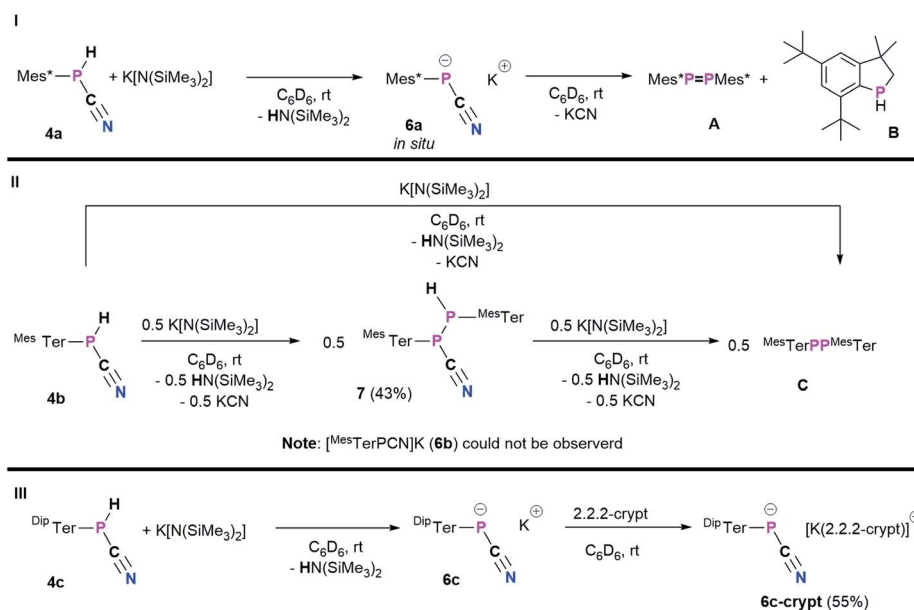
Fig. 4 Molecular structure of 5a. Hydrogen atoms (except H1) omitted and *t*Bu-groups on Mes\* rendered as wireframe for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): P1–C19 1.799(3), N1–C19 1.136(3), N1–B1 1.584(3), P1–C19–N1 175.7(2), C19–N1–B1 178.3(2), C19–P1–C1 97.71(11).

$[(R_2PPCN)^-]$ ; R = Ph, Cy, *t*Bu, *N*(*i*Pr)<sub>2</sub>) as counter-anions for anionic *cyclo*-triphosphido cobalt complexes.<sup>51</sup> Inspired by these results, the potential of 4a–c being deprotonated by K[N(SiMe<sub>3</sub>)<sub>2</sub>] (KHMDs) was investigated (Scheme 5).

As a starting point, the cyanophosphine Mes\*P(H)CN (4a) and KHMDs were combined on an NMR scale, accompanied by a color change from colorless to yellow and formation of a colorless precipitate. <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were immediately recorded and show that the main species at this

point showed a <sup>31</sup>P{<sup>1</sup>H} NMR signal at –146.2 ppm, which according to <sup>1</sup>H NMR spectroscopy does not bear a P–H function and HN(SiMe<sub>3</sub>)<sub>2</sub> (HMDS, δ(<sup>1</sup>H) = 0.10 ppm) was observed as well.<sup>20</sup> This indicated successful deprotonation to give [Mes\*PCN]K (6a).

Nevertheless, 6a is unstable at room temperature and after 16 h at room temperature, the <sup>31</sup>P{<sup>1</sup>H} NMR data revealed three signals at 493.2 (Mes\*PPMes\*, A),<sup>25</sup> –79.7, and –146.2 ppm, respectively.<sup>20</sup> The signal at –79.7 ppm is now the main species and was assigned to the known 3,3-dimethyl-5,7-di-*tert*-butylphosphindane (B).<sup>52</sup> Unfortunately, up to now all attempts to isolate, crystallize or trap 6a have not been successful and only crystals of A and B could be obtained. From a mechanistic point of view, we assume that deprotonation of 4a by KHMDs leads to the formation of HMDS and 6a, the latter then eliminates KCN to give a reactive phosphinidene intermediate capable of both dimerization to give A and capable of insertion of the phosphinidene fragment into one methyl group of one *tert*-butyl group of the Mes\* substituent to yield B.<sup>52</sup> Burg and Slota noted that the stability of species of the type RPHX is greatly enhanced by the steric profile of the substituent R.<sup>53</sup> Therefore, the terphenyl-based cyanophosphines 4b and 4c were expected to make the anions isolable. The reaction of <sup>Mes</sup>TerP(H)CN (4b) and KHMDs resulted in an immediate color change of the reaction mixture from colorless to yellow and precipitation of a colorless solid. Interestingly, the clean formation of <sup>Mes</sup>TerPP<sup>Mes</sup>Ter (C) (δ(<sup>31</sup>P{<sup>1</sup>H}) = 492.5 ppm) and HMDS were observed even when the reaction mixture is directly analyzed by NMR spectroscopy after reacting both substrates.<sup>20</sup> To get information whether any other phosphorus containing species can be observed (*e.g.* intermediate formation of a phosphinidene which dimerizes to C), 4b and 0.5 eq. of KHMDs were



Scheme 5 Reactivity of 4a–c towards KHMDs: (I) *in situ* synthesis of [Mes\*PCN]K (6a) and decomposition towards phosphindane A, diphosphene B and KCN; (II) synthesis of <sup>Mes</sup>TerP(H)P(CN)<sup>Mes</sup>Ter (7) or diphosphene C dependent on the used stoichiometry; (III) synthesis of [DipTerPCN]K (6c) and [DipTerPCN][K(2.2.2-crypt)] (6c-crypt).



combined and the solution was directly analyzed by NMR spectroscopy. Intriguingly, two doublet signals were observed in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at  $-78.2$  and  $-82.6$  ppm with a coupling constant of  $^1J_{\text{P,P}} = 326.6$  Hz. The corresponding  $^{31}\text{P}$  NMR spectrum revealed the existence of two doublets of doublets with additional coupling constants of  $38.3$  Hz and  $216.3$  Hz, respectively. In addition, a highly diagnostic doublet of doublet signal in the  $^1\text{H}$  NMR spectrum at  $3.97$  ppm confirms that the above mentioned coupling constants correspond to  $^1J_{\text{P,H}}$  and  $^2J_{\text{P,H}}$  coupling, thus the obtained molecule bears a unique P(H)–P moiety.<sup>20</sup> In accordance with the NMR data and high-resolution mass spectrometry, SC-XRD verified the formation of the diphosphane  $^{\text{Mes}}\text{TerP}(\text{H})\text{P}(\text{CN})^{\text{Mes}}\text{Ter}$  (**7**, Fig. S1†). Treatment of **7** with additional amounts of KHMDS then resulted in the clean conversion to give diphosphane **C** as shown by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. It is worth mentioning, that the reaction of **4a** with half an equivalent of KHMDS only leads to the described concomitant formation of **6a**, **A**, **B**, KCN, and HMDS with parts of **4a** remaining unreacted. Finally, the even bulkier cyanophosphine  $^{\text{Dip}}\text{TerP}(\text{H})\text{CN}$  (**4c**) was reacted with equimolar amounts of KHMDS, giving an immediate color change to yellow. A significantly shielded signal in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at  $-142.0$  ppm (*c.f.* *in situ* prepared **6a**:  $\delta(^{31}\text{P}\{^1\text{H}\}) = -146.2$  ppm;  $[(\text{NHP})\text{PCN}]\text{M}$ :  $\delta(^{31}\text{P}\{^1\text{H}\}) = -124$  to  $-84$  ppm<sup>50</sup>) indicated the formation of the corresponding cyanophosphide  $[\text{Dip}^{\text{Ter}}\text{PCN}]\text{K}$  (**6c**). **6c** proved to be stable in  $\text{C}_6\text{D}_6$  solution for at least one week at room temperature. Subsequently, the potassium cation could be sequestered by adding 2.2.2-cryptand to quantitatively give the ion separated salt  $[\text{Dip}^{\text{Ter}}\text{PCN}][\text{K}(2.2.2\text{-crypt})]$  (**6c-crypt**). The ion separation leads to the expected low-field shift in the  $^{31}\text{P}\{^1\text{H}\}$  NMR of approximately  $20$  ppm so that a signal at  $-120.7$  ppm is detected. In addition, the molecular structure of **6c-crypt** was determined by SC-XRD (Fig. 5).

The structural parameters of the  $\text{P}^{(-)}\text{CN}$  unit indicate that the negative charge is mainly located at the phosphorus, with a N1–C31 bond length of  $1.1585(19)$  Å ( $\Sigma r_{\text{cov}}(\text{C}\equiv\text{N}) = 1.14$  Å,<sup>30</sup> *c.f.*  $\text{Ph}_3\text{PC}(\text{H})\text{CN}$   $1.158(3)$  Å).<sup>54</sup> This is minimally longer than in

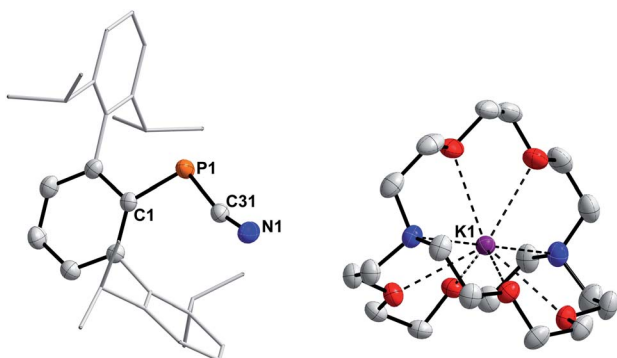


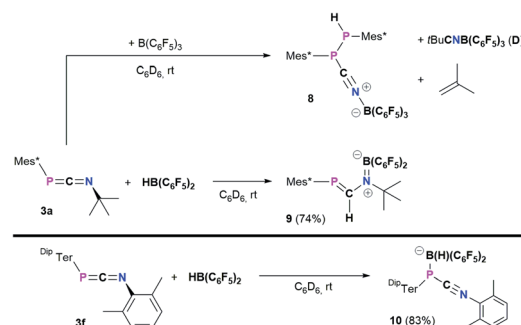
Fig. 5 Molecular structure of **6c-crypt**. Hydrogen atoms omitted and Dip-groups rendered as wireframe for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): P1–C31  $1.7680(14)$ , N1–C31  $1.1585(19)$ , P1–C31–N1  $165.45(12)$ , C1–P1–C31  $106.73(6)$ .

starting material **4a** ( $1.146(3)$  Å), whereas the P1–C31 bond length is slightly shortened ( $1.7680(14)$  Å; *c.f.* **4a**:  $1.793(2)$  Å). Therefore a major contribution from the resonance structure  $\text{R}^{(-)}\text{P}=\text{C}\equiv\text{N}$  and a minor contribution from the resonance structure  $\text{R}-\text{P}=\text{C}=\text{N}^{(-)}$  is reasonable, and is further supported by the C–N stretching frequency of  $2053\text{ cm}^{-1}$ . The only other structurally characterized cyanophosphides bear phosphorus based substituents at the phosphorus atom of the PCN moiety but show nearly identical bond lengths across the PCN axis (*c.f.*  $[\text{iPr}_2\text{PPCN}]^-$ : P–C  $1.763(1)$  Å, N–C  $1.160(2)$  Å;<sup>51</sup>  $[(\text{NHP})\text{PCN}]^-$ : P–C<sub>avg.</sub>  $1.75$  Å, N–C<sub>avg.</sub>  $1.16$  Å).<sup>50</sup> Whereas for the previously described cyanophosphides nearly linear arrangements of the PCN moieties are observed (N–C–P  $> 177^\circ$ ),<sup>50,51</sup> the P1–C31–N1 bond angle of  $165.45(12)^\circ$  deviates significantly from linearity which might be caused by steric repulsion of the sterically demanding  $\text{Dip}^{\text{Ter}}$  group.

### Reactivity of selected 1,3-phosphaazaallenes towards $\text{B}(\text{C}_6\text{F}_5)_3$ and Pier's borane $\text{HB}(\text{C}_6\text{F}_5)_2$

Heteroallenes like carbodiimides, isocyanates, and isothiocyanates have shown a diverse reactivity towards the perfluorinated boranes  $\text{B}(\text{C}_6\text{F}_5)_3$  and  $\text{HB}(\text{C}_6\text{F}_5)_2$  (Pier's borane), ranging from the development of new heterocycles to the formation of classic and frustrated Lewis pairs (FLPs) and 1,2-hydroboration reactions.<sup>41,55–58</sup>

Treatment of **3a** with  $\text{B}(\text{C}_6\text{F}_5)_3$  in toluene afforded a colorless suspension (Scheme 6, top). After stirring for 16 h and subsequent workup,<sup>20</sup> the isolated colorless solid was hardly soluble in aromatic hydrocarbons and started to polymerize tetrahydrofuran within minutes. From a saturated  $\text{C}_6\text{D}_6$  solution sufficient  $^1\text{H}$ ,  $^{11}\text{B}\{^1\text{H}\}$ ,  $^{19}\text{F}\{^1\text{H}\}$ , and  $^{31}\text{P}\{^1\text{H}\}$  data was obtained and the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum showed two characteristic signals at  $-46.8$  and  $-53.3$  ppm, respectively with a characteristic  $^1J_{\text{P,P}} = 247.5$  Hz coupling constant, reminiscent of  $^{\text{Mes}}\text{TerP}(\text{H})\text{P}(\text{CN})^{\text{Mes}}\text{Ter}$  (**7**) (*c.f.*  $\delta(^{31}\text{P}\{^1\text{H}\}) = -78.2$  and  $-82.6$  ppm,  $^1J_{\text{P,P}} = 326.6$  Hz). The existence of a P(H)–P moiety was supported by the  $^1\text{H}$  and  $^{31}\text{P}$  NMR data, which show that the signal at  $-53.3$  ppm is a doublet of doublets with  $^1J_{\text{P,H}} = 224.0$  Hz, which is further corroborated by a doublet signal with the same  $^1J_{\text{P,H}}$  coupling constant in the  $^1\text{H}$  NMR spectrum at  $5.44$  ppm. The reaction is accompanied by significant amounts of



Scheme 6 Reactivity of **3a** towards  $\text{B}(\text{C}_6\text{F}_5)_3$  and  $\text{HB}(\text{C}_6\text{F}_5)_2$ , and reactivity of **3f** towards  $\text{HB}(\text{C}_6\text{F}_5)_2$  to give **10**.



byproducts as evident from two signals in the  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum at  $-7.9$  (significantly broadened) and  $-20.7$  ppm, respectively. Similarly, the  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum shows a total of nine signals. Moreover, iso-butene was identified as byproduct ( $\delta(^1\text{H}) = 1.60$  and  $4.74$  ppm, Fig. S67 $\dagger$ ), similarly to the synthesis of the cyanophosphines **4a-c**.

Crystallization attempts gave two types of colorless crystals, and SC-XRD confirmed that indeed the diphosphane  $\text{Mes}^*\text{P}(\text{H})\text{P}(\text{CNB}(\text{C}_6\text{F}_5)_3)\text{Mes}^*$  (**8**, Fig. 6) was formed alongside the literature known nitrile-borane adduct  $t\text{BuCNB}(\text{C}_6\text{F}_5)_3$  (**D**) (Scheme 6, top).<sup>42</sup> It is worth mentioning, that all attempts to isolate **8** in pure fashion failed up to now, which is attributed to quite similar solubilities of **8** and **D**. In **8** the newly formed P1–P2 and N1–B1 bond lengths of  $2.2464(8)$  Å and  $1.572(3)$  Å are in good accordance with the formulation as single bonds ( $\Sigma r_{\text{cov}}(\text{P}-\text{P}) = 2.22$  Å;  $\Sigma r_{\text{cov}}(\text{N}-\text{B}) = 1.56$  Å).<sup>30</sup> The N1–C37 bond length of  $1.140(3)$  Å is a typical carbon nitrogen triple bond ( $\Sigma r_{\text{cov}}(\text{C}\equiv\text{N}) = 1.14$  Å),<sup>30</sup> and the P1,C37,N1,B1 axis is minimally bent (e.g. C37–N1–B1  $174.9(2)^\circ$ ).

All these metrics agree with phosphanitrilium borate **5a** (Fig. 4). It is noteworthy that the phosphaketene  $[\text{sP}]\text{PCO}$  reacted with  $\text{B}(\text{C}_6\text{F}_5)_3$  to give a zwitterionic diphosphirenium with a  $\text{P}_2\text{C}$  three-membered ring with an exocyclic  $\text{C}-\text{O}-\text{B}(\text{C}_6\text{F}_5)_3$  moiety.<sup>21</sup> We continued to investigate the reactivity of **3a** towards Pier's borane ( $\text{HB}(\text{C}_6\text{F}_5)_2$ ) to check its potential for hydroboration chemistry.<sup>59</sup>

The reaction of **3a** and  $\text{HB}(\text{C}_6\text{F}_5)_2$  yielded a yellow solid after workup (isolated yield 74%, Scheme 6, middle). Single crystals grown from layering a saturated  $\text{C}_6\text{D}_6$  solution with *n*-hexane revealed the product to be  $\text{Mes}^*\text{PC}(\text{H})\text{N}(\text{tBu})\text{B}(\text{C}_6\text{F}_5)_2$  (**9**, Fig. 7), showing that 1,2-hydroboration across the  $\text{C}=\text{N}$  bond of **3a** had occurred (Scheme 6, middle). Remarkably, the molecular structure of **9** reveals a novel heterodiene ( $\text{P}=\text{C}-\text{N}^{(+)}=\text{B}^{(-)}$ ) structural motif. Both, the P1–C19 and N1–B1 bond lengths of

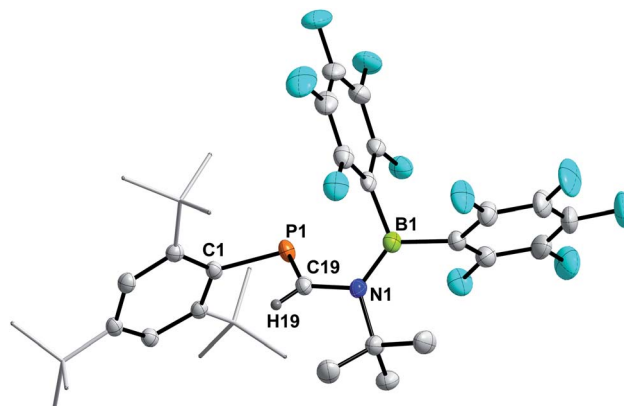


Fig. 7 Molecular structure of **9**. Hydrogen (except H19) omitted and *t*Bu-groups on  $\text{Mes}^*$  rendered as wireframe for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles ( $^\circ$ ): P1–C19  $1.6751(13)$ , N1–C19  $1.4278(15)$ , N1–B1  $1.3995(18)$ ; C1–P1–C19  $98.93(6)$ , P1–C19–N1  $123.69(9)$ , C19–N1–B1  $120.15(10)$ .

$1.6751(13)$  Å and  $1.3995(18)$  Å are best described as double bonds, respectively, which is also illustrated in the KS orbitals (PBE0-D3/def2-SVP, Fig. S91 $\dagger$ ). The HOMO is best described as the P–C and B–N  $\pi$ -bonds, respectively, with one node. The LUMO has  $\pi^*$  character for P–C and B–N bonds resulting in two nodes and with  $\pi$ -character between C and N, as expected for a heterodiene.<sup>60</sup> The nature of BN multiple bonds has been in the focus of recent computational studies,<sup>61,62</sup> and NBO results for **9** show a  $\sigma$  (N 79.5, B 20.5%) and  $\pi$  (N 86.1, B13.9%) NBO, which are mainly formed by the natural atomic hybrid orbitals located on N. This agrees well with the values obtained for 9,10-diimino-9,10-dihydro-9,10-diboraanthracene.<sup>62,63</sup> Topological analysis of the electron density using the QT-AIM approach revealed an electron density ( $\rho_{(3,-1)}$  [ $\text{e bohr}^{-3}$ ]) of 0.198 at the BN bond critical point (BCP), as well as an electron density Laplacian ( $\nabla^2$  [ $\text{e bohr}^{-5}$ ]) of 0.651, which corresponds nicely with the aforementioned dimindiboraanthracene.<sup>20,62</sup> In addition, the sum of angles around C19, N1, and B1 all add up to over  $359.8^\circ$ , in line with  $\text{sp}^2$ -hybridization. The solution NMR spectra of **9** are indicative that this diene structure sustains in solution, with one resonance in the  $^{11}\text{B}$  NMR spectrum at 36.4 ppm, indicating a tri-coordinated boron atom (cf.  $(\text{C}_6\text{F}_5)_2\text{BNMe}_2$  33.7 ppm).<sup>64</sup> Given the double bond character of the  $\text{B}=\text{N}$  bond, two distinct  $\text{C}_6\text{F}_5$  groups are detected giving two sets of signals in the  $^{19}\text{F}$  NMR spectrum. Highly diagnostic is the  $^1\text{H}$  NMR chemical shift of the  $\text{P}=\text{C}(\text{H})$  proton at 7.80 ppm as a doublet with a  $^2J_{\text{P,H}}$  coupling constant of 18.5 Hz (cf.  $\text{Mes}^*\text{P}=\text{C}(\text{H})\text{N}(\text{SiMe}_3)_2$  (ref. 65)  $\delta(^1\text{H}) = 8.24$  (d,  $^2J_{\text{P,H}} = 16.8$  Hz)). The aforementioned  $^1\text{H}$  NMR signal, the deshielded  $^{31}\text{P}\{^1\text{H}\}$  NMR signal at 228.5 ppm and the  $^{13}\text{C}\{^1\text{H}\}$  NMR signal of the  $\text{P}=\text{C}(\text{H})$  functionality ( $\delta^{13}\text{C}\{^1\text{H}\} = 177.5$  ppm,  $^1J_{\text{P,C}} = 37.3$  Hz) clearly indicate a phosphalkene (cf. 2,6-( $\text{Mes}^*\text{P}=\text{C}(\text{H})$ ) $_2(\text{NC}_5\text{H}_5)$   $\delta(^{31}\text{P}) = 249.1$  ppm).<sup>66</sup> Interestingly, carbodiimides react with Pier's Borane to the corresponding four-membered boron amidinates.<sup>55</sup> Similar four-membered heterocycles are formed when isothiocyanates are treated with  $\text{HB}(\text{C}_6\text{F}_5)_2$ .<sup>41</sup>

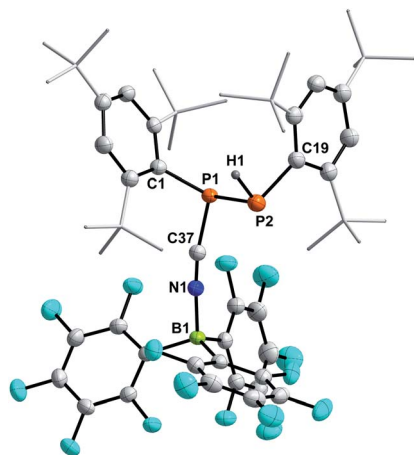


Fig. 6 Molecular structure of **8**. Hydrogen atoms (except H1) omitted and *t*Bu-groups on  $\text{Mes}^*$  rendered as wireframe for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles ( $^\circ$ ): P1–P2  $2.2464(8)$ , N1–B1  $1.572(3)$ , P1–C37  $1.784(2)$ , P1–C1  $1.844(2)$ , P2–C19  $1.852(2)$ , N1–C37  $1.140(3)$ ; P1–C37–N1  $165.4(2)$ , C37–N1–B1  $174.9(2)$ .



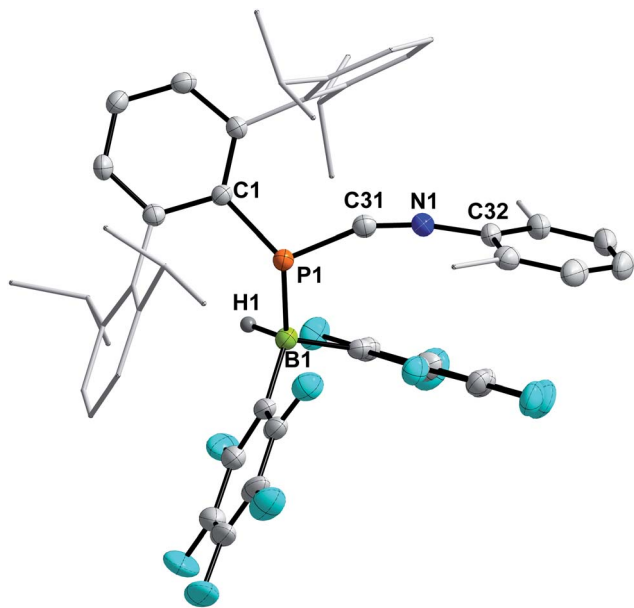


Fig. 8 Molecular structure of **10**. Hydrogen (except H1) omitted and Dip and Xyl groups rendered as wireframe for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): P1–C31 1.754(3), N1–C31 1.161(3), P1–B1 2.060(3); P1–C31–N1 157.7(2).

Finally, the influence of the substitution pattern at both the phosphorus and nitrogen atoms was investigated exemplarily by reacting the 1,3-phosphaazaallene **3f** (bearing <sup>Dip</sup>Ter and Xyl substituents) with HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (Scheme 6, bottom). One singlet signal in the <sup>11</sup>B{<sup>1</sup>H} NMR spectrum at –19.3 ppm, indicated a four-coordinate boron atom. In contrast to **9**, only three signals are observed in the <sup>19</sup>F{<sup>1</sup>H} NMR spectrum and the <sup>31</sup>P{<sup>1</sup>H} signal is observed at –83.1 ppm, over 300 ppm shifted towards higher field when compared to **9**. These data together with the data obtained by SC-XRD showed that instead of 1,2-hydroboration, the Lewis acid base adduct <sup>Dip</sup>TerP(HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>)CNXyl (**10**) with a newly formed P–B bond was obtained (Fig. 8). The C1–N1 bond length of 1.161(3) Å is shortened by approximately 0.04 Å when compared to the starting material **3f** (*c.f.* 1.2009(15) Å) and is now close to a carbon nitrogen triple bond ( $\Sigma r_{\text{cov}}(\text{C}\equiv\text{N}) = 1.14 \text{ Å}$ ).<sup>25</sup> Accordingly, the C31–N1–C32 bond angle increases to 165.1(3)° (*c.f.* 143.24(12)° (**3f**)). The P1–C31 bond length of 1.754(3) Å also increases compared to **3f** (1.6785(12) Å) indicative of a single bond (*c.f.* <sup>Dip</sup>TerP(H)CN **4c** 1.793(2) Å). The P1–B1 bond length of 2.060(3) Å is 0.1 Å longer than the respective sum of the covalent radii ( $\Sigma r_{\text{cov}}(\text{P–B}) = 1.96 \text{ Å}$ )<sup>25</sup> and corresponds with dative bonding as further ascertained by a low WBI for the P–B bond of 0.85.

## Conclusions

Phospha-Wittig reagents have been shown to react with isocyanides to give 1,3-phosphaazaallenes **3a–f**. In case of the CN*t*Bu-derivatives these were further transformed in the corresponding cyanophosphines **4a–c**. CN*t*Bu acts in this case as a disguised HCN transfer reagent. This allowed the structural

characterization of this underrepresented class of phosphines and deprotonation yielded in one case a rare example of an aryl-substituted cyanophosphide anion. Moreover, **3a** was shown to be 1,2-hydroborylated along the C=N bond to give the unique heterodiene **9** with alternating PC and BN double bonds. Studies using cyanophosphide **6c** as a ligand and exploiting heterodiene **9** in FLP-type chemistry are currently underway.

## Data availability

All experimental, crystallographic and computational data are provided in the ESI.

## Author contributions

M. F. discovered and optimized the formation of 1,3-phosphaazaallenes, studied the scope and studied the reactivity of compounds **3a–f**. M. F. prepared the experimental part and the first draft of the manuscript. C. H.-J. designed the overall research, supervised the work, carried out the computational work, contributed to IR analysis, finalized the manuscript, proofread the experimental part and coordinated the overall project.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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