ChemPubSoc Europe

DOI: 10.1002/ejic.201501017

EurJIC European Journal of Inorganic Chemistry

Full Paper

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Phosphaalkenes

Direct Access to Inversely Polarized Phosphaalkenes from Elemental Phosphorus or Polyphosphides

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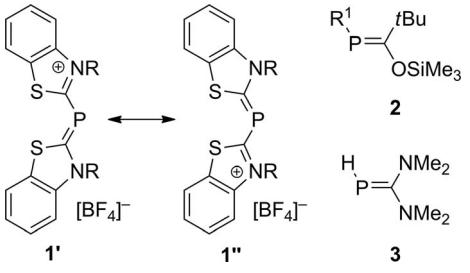
Abstract: Phosphorus-containing multiple-bond systems have received great interest in various applications but often require elaborate syntheses and special precursors. In this paper, we describe simple methods for the synthesis of imidazoyl phosphinidenes and bis(imidazolyl)–P(I) halides from elemental phosphorus or the heptaphosphides Na_3P_7 and $(Me_3Si)_3P_7$. The reactions of imidazolium salts with KO*t*Bu and P_4 afford mixtures of imidazoyl phosphinidenes and P_n compounds and, for N-methylated imidazolium salts, also bis(imidazolyl)–P(I) halides. NMR spectroscopy studies revealed the formation of a bis(imidazoyl)-substituted tetraphosphatriene and the bicyclic anion HP_4^- as transient intermediates and indicated the participation of *t*BuOH in the formation of imidazoyl phosphinidenes. Na_3P_7 and $(Me_3Si)_3P_7$ can be obtained from P_4 and P_{red} in excellent yields by a safe and simple method and are versatile precursors for the synthesis of imidazoyl phosphinidenes with varying steric demand.

Introduction

Phosphorus-containing multiple-bond systems have experienced an amazing evolution during recent decades: included in the elusive "nonexistent compounds" up to the 1960s,[1] they can now be considered one of the most advanced classes of compounds with π-bonds between heavier main-group elements,[2] and their application is receiving interest in diverse fields such as catalysis[3] and π-conjugated materials.[4] A prerequisite for this development was that chemists learned to overcome the low π-bond stability that renders multiple-bond systems unstable with respect to dimerization or addition reactions.[2] This is often achieved by introducing sterically protecting substituents (kinetic stabilization),[5] electronic stabilization by π delocalization or a combination of both. Prototypes illustrating the stabilization of phosphorus-containing double-bond systems include phosphamethine cyanines **1**[6] (the first isolable phosphorus–carbon multiple-bond systems ever prepared) and the first isolable acyclic phosphaalkene **2** (Scheme 1).[8] The stability of **1** is generally related to the π delocalization associated with the resonance between canonical structures **1′** and **1″**,[6] but the presence and delocalization of charge may also play a role.[7]



Scheme 1. Prototypes of phosphorus-containing double-bond systems: phosphamethine cyanines (**1**, R = Me, Et) and phosphaalkenes **2** (R^1 = Me, Cy, *t*Bu, Ph) and **3**.

The stability of **2** may be related to a combination of steric protection and the attenuation of the phosphorus electrophilicity by the π-donating siloxy group. This π-donor stabilization can be increased by introducing two donating amino groups to afford **3**,[9] which is stable even in the absence of steric shielding.

The need to provide sufficient protection for the π-bonds implies that phosphorus-containing multiple-bond systems must often be accessed by elaborate, multistep syntheses or through the utilization of specially designed precursors, which may be laborious to prepare. In this work, we report the synthesis of sterically unprotected low-coordinate phosphorus compounds with similar structures to those of **1** and **3** in a one-step process involving the direct activation of white phosphorus.[10] As an alternative entry to these compounds, we also report a simple and safe synthesis of the heptaphosphides Na_3P_7 and $(Me_3Si)_3P_7$.

Our studies were inspired by the ground-breaking reports by the group of Bertrand on the activation of P_4 with various types of stable amino-substituted carbenes.[11–15] Depending on the

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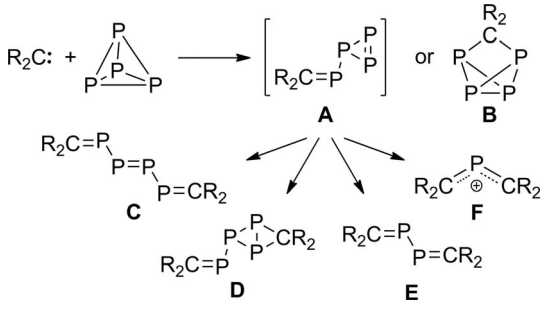
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201501017.

steric demand and "philicity" of the carbenes, these reactions yield transient cyclic diphosphenes **A**[11] or polycycles **B**[14] as initial products (Scheme 2). The former are not directly observable but can be trapped by cycloaddition with a diene or an excess of the carbene.[11,13] The trapping products **C** and **D** may in turn undergo further aggregation or reaction with P_4 to yield species with P_8 or P_{12} scaffolds.[12,14] With less bulky carbenes, the fragmentation of the P_4 skeleton to afford products with P_1 to P_3 cores (e.g., structures **E** and **F**) has also been observed.[13] We have now modified this approach by replacing the preformed carbene with a mixture of an imidazolium salt and a strong anion base. Although the combinations of these reagents produces N-heterocyclic carbenes (NHCs),[16] their reactivity towards P_4 does not simply mirror the previously reported behaviour of NHCs[11–14] but offers access to a new and unprecedented reaction channel under these conditions.

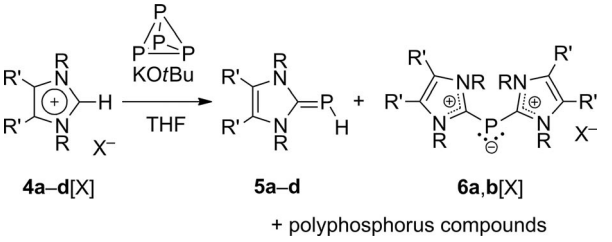


Scheme 2. Pathways for the breakdown of P_4 by reaction with various types of stable carbenes (R_2C = cyclic or acyclic diaminocarbenes, cyclic amino alkyl carbenes or diaminocyclopropylidene).[11–14]

Results and Discussion

Three-component reactions between white phosphorus and equimolar amounts of an imidazolium salt and KO*t*Bu were conducted either by dissolving all of the components together or by reacting the imidazolium salt and the base first to give an NHC and *t*BuOH and then adding P_4. Tetrahydrofuran (THF) was the most suitable solvent, but the reactions also occurred in diethyl ether or toluene. The resulting mixtures were stirred for 12 to 24 h to give suspensions, which were separated by filtration. The analysis of the supernatant solutions and the reddish precipitates by solution or solid-state ^{31}P NMR spectroscopy indicated that the product distribution depends on the N substituents of the imidazolium salt but not on the order in which the components are added.

For the N-methylated derivatives **4a**[I] and **4b**[I], the supernatant solutions contained phosphaalkenes **5a** and **5b** (Scheme 3) as the dominant products. In addition, ^{31}P NMR spectra recorded with long acquisition times revealed low-intensity signals with complex splitting patterns, which indicated the presence of soluble, unidentified polyphosphorus compounds. In some reactions, minor amounts of the cations **6a** and **6b** (see below) were also detected. In addition to inorganic salts, the reddish precipitates contained ionic **6a**[I] and **6b**[I] as the major phosphorus-containing components. Species of this type are analogues of the phosphamethine cyanine **1**[6] but have also been addressed as bis(carbene) complexes of a univalent P(I) cation.[17,18] In addition, solid-state ^{31}P and ^{13}C NMR spectroscopy studies disclosed the presence of species tentatively assigned as organic polyphosphorus compounds.



Scheme 3. Products observed in the reactions of imidazolium salts **4a**–**4d**[X] with P_4 and KO*t*Bu (**4a**[X]–**6a**[X]: X = I, R = Me, R′ = H; **4b**[X]–**6b**[X]: X = I, R = Me, R′ = Me; **4c**[X]–**5c**: X = Cl, R = mesityl, R′ = H; **4d**[X]–**5d**: X = Cl, R = 2,6-diisopropylphenyl, R′ = H).

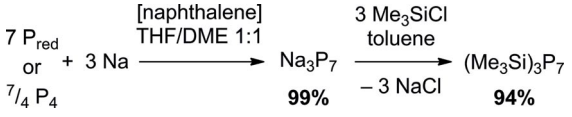
In the reactions of the N-arylated imidazolium salts **4c**[Cl] and **4d**[Cl], the phosphaalkenes **5c** and **5d** as well as soluble and insoluble organophosphorus materials were observed but bis(carbene)-stabilized P(I) cations were not. Presumably, their formation is disfavoured by the higher steric demand of the *N*-aryl substituents. Phosphaalkene **5d** has been prepared previously by phosphinidene transfer from a phosphasilene to a carbene,[19] the reaction of imidazolium salts with Na(OCP) or $(Me_3Si)_3P_7$,[20] or the methanolysis of a P-silylated precursor.[24]

The phosphaalkenes ("imidazoyl phosphinidenes") **5a**–**5c** were separated by evaporation of the supernatant solutions and extraction of the residue with benzene and purified by sublimation. Phosphaalkene **5d** was identified only by spectroscopic data but could not be isolated. The salts **6a**[I] and **6b**[I] were isolated by extraction of the precipitate with CH_2Cl_2 and crystallization. The salt **6a**[I] was further converted to **6a**[OTf] (OTf = triflate) by anion exchange with Me_3SiOTf. The yields with respect to **4a**[I] obtained under optimized reaction conditions of **5a** (23 %) and **6a**[I] (50 %) indicate that both species are formed in roughly equimolar amounts and that 73 % of the imidazolium salts are converted into these products. Even though no formation of **6c**[Cl] was observed in the reaction of **4c**[Cl], the phosphaalkene **5c** was isolated in a similar yield of 25 %.

As white phosphorus is dangerous to handle and difficult to obtain commercially, we investigated different routes to these phosphaalkenes. Na(OCP) and $(Me_3Si)_3P_7$ have been used previously as phosphorus sources in their synthesis.[20,21] However, this approach is limited to N-arylated derivatives. The *N*-methyl- and *N*-isopropylimidazolium iodides or chlorides do not react with Na(OCP) or $(Me_3Si)_3P_7$ even at temperatures above 80 °C. Furthermore, the literature-known synthesis of $(Me_3Si)_3P_7$ relies on the use of Na/K alloy, a dangerous reagent unsuitable for large-scale synthesis.[22] The first step in this procedure is the formation of the trimetallated P_7 cage, which led us to explore the direct use of trimetal heptaphosphides for the synthesis of imidazoyl phosphinidenes.

To circumvent the use of Na/K alloy in the heptaphosphide synthesis but still achieve a high conversion rate in the reaction between sodium and elemental phosphorus, we employed cat-

alytic amounts of naphthalene. Thus, sodium can be used as the only reductant, and Na_3P_7 is obtained in quantitative yield by simply stirring a suspension of white phosphorus, elemental sodium, and naphthalene (1 mol-% per P) in a 1:1 mixture of dimethoxyethane (DME) and THF for 3 d at 20 °C (Scheme 4). It can also be obtained in equally high yields from red phosphorus. In that case, the suspension has to be stirred for 2 d at 20 °C and then heated under reflux for 24 h. In both cases, the orange Na_3P_7 was collected by filtration, washed with *n*-hexane and dried thoroughly. Note that even after 3 d under reduced pressure and elevated temperature (70 °C), the product still contains 12 mol-% DME.

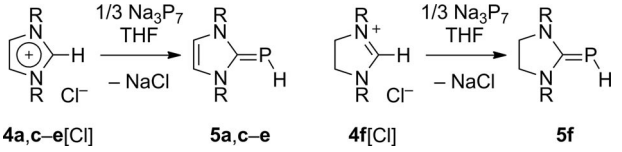


Scheme 4. High-yielding, safe and simple synthesis of Na_3P_7 and $(Me_3Si)_3P_7$ from elemental phosphorus by employing catalytic amounts of naphthalene.

The insoluble Na_3P_7 can be converted to soluble $(Me_3Si)_3P_7$ in 94 % yield by treating it with trimethylsilyl chloride in toluene at –80 °C, followed by filtration to remove the NaCl byproduct and recrystallization from toluene.

We found Na_3P_7 to be a versatile phosphorus source for the synthesis of imidazoyl and imidazolidinyl phosphinidenes. The treatment of suspensions of the imidazolium salts **4a**[Cl] and **4c**[Cl]–**4f**[Cl] in THF with Na_3P_7 followed by extraction with toluene and recrystallization or sublimation gives the phosphaalkenes **5a** and **5c**–**5f** in 60 to 80 % yield based on the imid~azolium salts (Scheme 5). The procedure works equally well for N-alkylated and N-arylated imidazolium salts, and the only difference is that the former need to be heated under reflux for 16 h, whereas the latter react at 20 °C. Imidazoyl phosphinidene **5a** can also be obtained from the imidazolium iodide **4a**[I], albeit in considerably lower yield (25 vs. 71 %).

The reaction products **5a**–**5f** and **6a**[I] and **6b**[I] were identified unambiguously from analytical and spectroscopic data. The phosphaalkenes **5a**–**5c** and **5e** exhibit more shielded ^{31}P NMR resonances (δ = –147 to –149 ppm) compared with those of the previously reported **5d** (δ = –136.7 ppm, Table 1).[20] The same trend in the ^{31}P NMR shifts was observed by Bertrand and co-workers for imidazoyl phenylphosphinidenes and attributed to the different π-accepting properties of the carbenes.[23] Although the ^{31}P NMR resonances of all five species are considerably more shielded than those of acyclic *C*-amino phosphaalkenes (cf. $\delta^{31}P$ = –62.6 ppm for **3**),[9] the presence of a P–C double bond is corroborated by the deshielded ^{13}C NMR resonance of the α-carbon atom ($\delta^{13}C$ = 178 to 181 ppm). The ^{13}C and ^{1}H NMR spectra show only one set of resonances for the nuclei of the CH/CMe and NR units on both sides of the P–C double bond; therefore, the barrier for the *E*/*Z* isomerization is very low.



Scheme 5. Synthesis of N-alkylated and N-arylated imidazoyl phosphinidenes **5a** and **5c**–**5e** from the corresponding imidazolium chlorides and Na_3P_7. The imidazolidinyl phosphinidene **5f** can be obtained in the same way from the dihydroimidazolium chloride **4f**[Cl]; R = Me (**4a**, **5a**), mesityl (**4c**, **5c**), 2,6-diisopropylphenyl (**4d**,**f**, **5d**,**f**), *i*Pr (**4e**, **5e**).

The ^{31}P NMR signals of the cations **6a** and **6b** ($\delta^{31}P$ = –113 to –117 ppm) are less shielded than those of the neutral **5a**–**5d** and match those of known acyclic bis(NHC)–P(I) cations.[17] The ^{31}P magic-angle spinning (MAS) NMR spectra of the insoluble residues contain a broad, featureless resonance between δ = –200 to 200 ppm and a maximum at δ ≈ –2 ppm. The extension of this signal reflects the wide range of chemical shifts known for polyphosphorus frameworks,[25] and the inability to resolve individual signals points to a highly disordered structure with a low degree of crystallinity. The ^{13}C MAS spectra of the insoluble solids contain similarly broadened resonances. The observed chemical-shift patterns indicate the presence of NHC units together with minor amounts of other unidentified structural motifs. Further assignments, in particular of a possible connection between the carbon and phosphorus building blocks, remained elusive.

The structural assignments derived from the spectroscopic studies were confirmed by single-crystal XRD studies of **5a**–**5c** as well as **6a**[OTf][26] and **6b**[I]. For **5c**, a qualified discussion of the metrical parameters is impeded by an orientational disorder, which becomes evident in an elongation of the thermal ellipsoid of the P1 atom along the direction of the P–H bond and the location of the P-bound hydrogen atom at a split position on either side of the P1–C1 bond (see Figure S9 in the Supporting Information). We interpret these peculiarities as resulting from the superposition of two molecules with different

Table 1. Comparison of ^{31}P NMR shifts [ppm] and $^{1}J_{P,H}$ coupling constants [Hz] as well as selected bond lengths [Å] and angles [°] of the imidazoyl phosphinidenes **5a**–**5e**, **7** and **8** (in C_6D_6); Dipp = 2,6-diisopropylphenyl; Mes = mesityl.

	5a	**5b**	**5c**	**5d**[19]	**5e**	**7**[27]	**8**[27]
R	Me	Me	Mes	Dipp	*i*Pr	Dipp	Dipp
R′	H	Me	H	H	H		
$\delta(^{31}P)$	–149.3	–148.8	–147.3	–136.7	–149.9	–143.0	–129.5
$^{1}J_{P,H}$	165	165	165	164	166	171	–
C=P	1.763(3)	1.772(1)[a]	1.747(2)	1.752(1)		1.763(2)	1.774(1)
N–C–N	104.9(2)	105.1(1)[a]	104.3(2)[b]	104.3(1)		103.7(2)	103.8(1)
N–C–P	124.0(2)	124.6(1)	127.7(2)	123.9(1)		127.2(2)	119.9(1)
	131.2(2)	130.2(1)[a]	128.0(2)[b]	131.8(1)		129.1(2)	135.8(1)

[a] The crystal structure contains a second (disordered) molecule with the following parameters: C=P 1.774(2) Å, N–C–N 105.4(2)°, N–C–P(avg.) 127.3(1)°. [b] Average values for two disordered molecules.

orientations of the PH unit. This hypothesis is corroborated by the fact that the P–C–N bond angles lack a pronounced dissymmetry (vide infra) but are indistinguishable within experimental error. A similar disorder phenomenon is also observed for one of two crystallographically independent molecules in crystalline **5b** (Figure S10).

A comparison of selected bond lengths and angles for different imidazoyl phosphinidenes is given in Table 1. The molecular structures of **5a** (Figure 1) and the ordered molecule of **5b** feature a planar arrangement of all heavy atoms and the (freely refined) H1 atoms (largest deviations from least-squares plane 0.012 and 0.018 Å for H1 in **5a** and **5b**, respectively). The P=C distances [**5a**: 1.763(3) Å, **5b**: 1.772(1) Å] differ insignificantly from those in **5d** [1.752(1) Å][20] or C-lithiated **7** [Scheme 6, 1.763(2) Å].[27] All P=C distances are close to the upper limit of reported double-bond lengths in *C*-aminophosphaalkenes (1.70 to 1.76 Å);[28] a marginally longer bond was reported recently for the *P*-silylated derivative **8** [Scheme 6, 1.774(1) Å].[24] The bond lengths in the N-heterocyclic ring as well as the N–C–N and N–C–P angles of **5a**, **5b** and **5d** are nearly identical. The C–P–H angles [**5a**: 96(1)°, **5b**: 96(2)°] are also similar to that in **5d** [94.5(7)°][20] and somewhat more acute than that in **7** [102(2)°].[27] The substantial difference between the P–C–N angles at the *E* and *Z* positions relative to the P–H bond [**5a**: 124.0(2) vs. 131.2(2)°; **5b**: 124.6(1) vs. 130.2(1)°] is a typical feature of P=C double-bond systems.[28] Consequently, the significantly different steric and electronic properties of the imidazoyl units are not reflected in the structural data of the phosphaalkenes **5a** and **5d**. We previously observed the same feature when comparing the structural data of **5d** to **5f**, which bears a saturated imidazolidinyl unit with a CH_2–CH_2 bridge in the NHC backbone.[21]

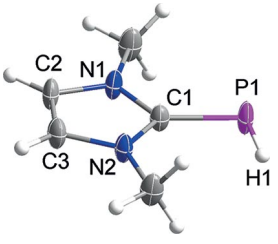


Figure 1. Molecular structure of crystalline **5a**. Thermal ellipsoids are drawn at 50 % probability level. Selected bond lengths [Å] and angles [°]: P1–C1 1.763(3), P1–H1 1.32(3), N1–C1 1.361(3), N1–C2 1.388(3), C1–N2 1.368(3), N2–C3 1.389(3), C2–C3 1.336(4), C1–P1–H1 96(1), N1–C1–N2 104.9(2), N1–C1–P1 124.0(2), N2–C1–P1 131.2(2).

Scheme 6. Related imidazoyl phosphinidenes **7**[27] and **8**[24] and a related bis(NHC)–P(I) cation **9**;[17] R = 2,6-diisopropylphenyl.

Crystalline **6a**[OTf] and **6b**[I] contain two or one crystallographically independent $[P(NHC)_2]^+$ cations (Figures 2 and S11), which connect to the triflate or iodide anions through weak CH···X (X = F, I) and CH···O hydrogen-bond interactions. The structural characteristics of the cations resemble those of **9**[17] (Scheme 6) and feature bent C–P–C units and helical conformations, which result from a twist of the heterocyclic rings relative to the central PC_2 plane. The P–C bond lengths [1.796(1) to 1.804(2) Å] are slightly shorter than those in **9** [1.824(2)/1.823(2) Å[17]], whereas the C–P–C angles [96.3(1) to 98.2(1)°] are similar [97.4(1)°].[17] The cations differ from each other and from **9** mainly in the twist angles between the PC_2 and NHC planes [interplanar angles 36.2(1) to 47.5(1)° for **6a** and 42.7(1) and 43.5(1) for **6b** vs. ca. 50 to 60° for **9**].[17,29] The perceptibly smaller twists in **6a** and **6b** compared with that in **9** may be attributed to the smaller *N*-alkyl substituents.

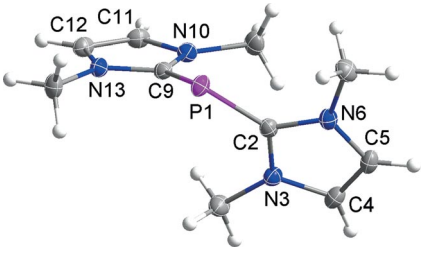
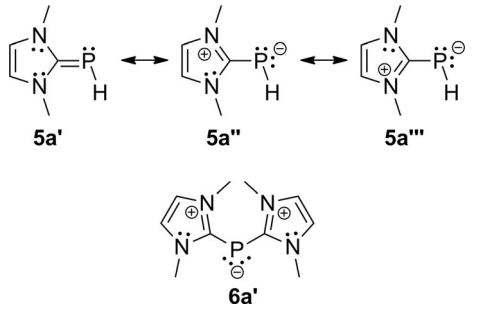


Figure 2. Molecular structure of one of the cations of crystalline **6a**[OTf]. Thermal ellipsoids are drawn at 50 % probability level. Selected bond lengths [Å] and angles [°] (the values in brackets refer to the second crystallographically independent unit; the data for **6b**[I] are given in the Supporting Information): P1–C9 1.797(1) [1.800(1)], P1–C2 1.796(1) [1.796(1)], C2–N3 1.357(2) [1.356(2)], C2–N6 1.350(2) [1.351(2)], N3–C4 1.384(2) [1.378(2)], N3–C8 1.461(2) [1.461(2)], C4–C5 1.349(2) [1.343(2)], C5–N6 1.381(2) [1.385(2)], N6–C7 1.464(2) [1.462(2)], C9–N13 1.356(2) [1.353(2)], C9–N10 1.361(2) [1.357(2)], N10–C11 1.385(2) [1.381(2)], N10–C15 1.462(2) [1.462(2)], C11–C12 1.345(2) [1.344(3)], C12–N13 1.385(2) [1.381(2)], N13–C14 1.464(2) [1.463(2)], C9–P1–C2 98.2(1) [96.3(1)].

For species with similar molecular structures to those of **5a** and **6a** (e.g., **5d**,[20] **7**,[27] or P-silylated **8**),[20] P–C distances in the range of single bonds are commonly observed. This observation has raised a vivid debate on the nature of the P–C bonding, and compounds of type **5** are described either as inversely polarized phosphaalkenes with a polarized covalent σ-bond and an inversely polarized π-bond[28] or as phosphinidene–NHC adducts featuring a superposition of two dative bonds.[30] The observed structural and spectroscopic features of **5a** are in accordance with the results of a recent computational study,[31] which depicts the bonding in terms of the leading resonance structures **5a′**–**5a‴** (Scheme 7). This description is an exact match of the picture invoked for inversely polarized phosphaalkenes,[28] but computational predictions of relatively low dissociation energies for the P–C bond indicate that these compounds may present a borderline case. For **6a**, a natural bond order (NBO) analysis suggests that a canonical structure **6a′** is the leading resonance structure. However, a second-order perturbation analysis indicates that hyperconjugation between the phosphorus lone pairs and the adjacent π*(CN) orbital exerts a similar stabilizing effect to the π conjugation in the NCN unit of the heterocycle and, thus, suggests that the central CPC unit still exhibits a substantial π-bonding contribution regardless of its torsional distortion.

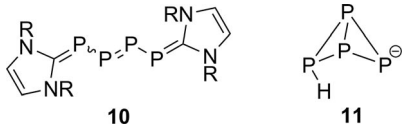


Scheme 7. Leading resonance structures of **5a**[31] and **6a**.

The formation of comparable molar quantities of **5a** and **5b** as well as **6a** and **6b** in the reactions between P_4, *t*BuOH, and the appropriate imidazolium salts reveals a formal parallel to the well-known disproportionation of P_4 in alkaline medium to give phosphane and hypophosphorous acid: $P_4 + 4H_2O \rightarrow 2PH_3 + 2H_3PO_2$.

However, as the formation of the phosphaalkenes **5c** and **5d** is not accompanied by the generation of detectable amounts of phosphamethine cyanines (which suggests that both products are formed through independent routes) and the occurrence of a substantial amount of insoluble phosphorus-containing material in all reactions has to be accounted,[32] we must assume that the reactions reported here follow a different pathway. To cast light on the formation of **5**, we studied the reactions of the imidazolium salts **4a**[I] and **4c**[Cl] with P_4 and *t*BuOK at low temperature through ^{31}P NMR spectroscopy.

The treatment of **4c**[Cl] with P_4 and *t*BuOK at –20 °C gave a solution with a ^{31}P NMR spectrum that showed the signals of **5c**, unreacted P_4, and two transient AA′XX′ patterns in a ratio of ca. 4:1 (see Figure S7). The parameters derived from spectral simulation of the signals of the more abundant component [$\delta^{31}P$ = 451.3 (AA′), 43.7 ppm (XX′) $J_{A,A'/X,X'}$ = –498/±34 Hz; $J_{A,X/A,X'}$ = –382/288 Hz][33] closely resemble those of the tetraphosphatrienes of Bertrand (**C**, Scheme 2),[11,12] and we assign the observed intermediates as the *N*-mesityl derivatives *E*/*Z*-**10** on this basis (Scheme 8).[33] The formation of these species was explained[11,12] as resulting from the sequential attack of two nucleophilic carbenes on P_4 during the initial stages of the reaction. Although analogous derivatives were unobservable in the reaction of **4a**[I] (presumably as their lifetimes are much shorter owing to the lower steric demand of the N substituents), the activation of white phosphorus by sterically less demanding carbenes may give rise to cationic P(I)–bis(carbene) adducts (**F**, Scheme 2).[13] Consequently, the formation of **6a** and **6b** in the reaction of P_4 with **4a**[I]/**4b**[I] and *t*BuOH can support the interpretation that this transformation is likewise initiated by carbene-activation of P_4.



Scheme 8. Transient intermediates *E*/*Z*-**10** (R = mesityl) and **11**[40] observed during the reactions of imidazolium salt and /KO*t*Bu with P_4.

As previous accounts on reactions of P_4 with carbenes do not mention the observation of analogues of **5a**–**5d**,[11–14] we attribute their formation to the participation of *t*BuOH, which is a byproduct of the deprotonation of imidazolium salts and is not separated in the reactions reported here. This conjecture is supported by the finding that the formation of **5a** is suppressed if the deprotonation of the imidazolium salt is performed with sodium hydride.[34] It is corroborated further by the outcome of experiments conducted with deuterium-labelled isotopomers of **4a**[I] as starting materials. The most decisive results were obtained from studies involving [D_3]**4a**[I], in which all three ring-carbon atoms were uniformly deuterated. In this case, the reactions produced a blend of isotopomers [D_n]**5a** (n = 1 to 3; detected by analysis of the ^{31}P NMR spectra of the reaction mixtures, Figure 3, a), which feature both P–D and P–H substitution. This product distribution can be consistently explained if we assume that the P–D isotopomers arise from proton-transfer reactions with *t*BuOD (formed by the initial deprotonation of the deuterated imidazolium salt) and that the P–H isotopomers arise from reactions with residual protic impurities that dilute the isotope labels. This hypothesis was corroborated by the observation that the fraction of P–H isotopomers increased substantially if the reaction was conducted in a solvent that had previously been deliberately treated with a drop of H_2O (Figure 3, b).[35,36]

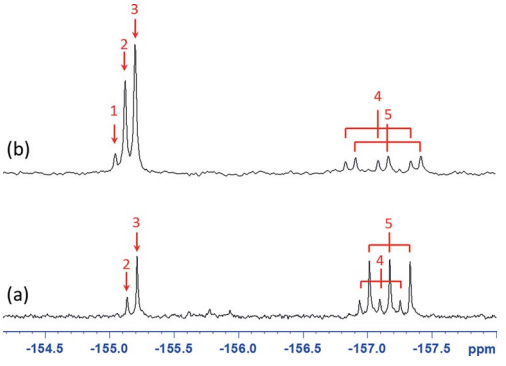


Figure 3. Expansion of the ^{31}P NMR spectra of solutions obtained from the reaction of [D_3]**4a**[I] with KO*t*Bu and P_4 in (a) THF and (b) THF with a drop of H_2O. The shown signals are attributable to the H and D isotopomers of **5a** (1: H_2-NHC=PH, 2: HD-NHC=PH, 3: D_2-NHC=PH, 4: HD-NHC=PD, 5: D_2-NHC=PD). Note that the spectra were recorded at different magnetic field strengths (101.2 vs. 161.9 MHz); thus, the $^1J_{P,D}$ couplings have different scaling.

Similar experiments on substrates with specific isotope labels at the 2- ([D_1]**4a**) or 4,5-positions of the ring ([D_2]**4a**) gave less conclusive results. In this case, the known propensity of NHCs or NHC/imidazolium mixtures to exchange their ring H atoms with protic solvents or substrates[37,38] led to scrambling of the isotope labels during the reaction, which precluded further mechanistic interpretation. This exchange can also explain the formation of CH-protonated products from [D_3]**4a**.

As the deuteration experiments allowed us to identify the imidazolium ions as the initial source of (at least part of) the P-bound hydrogen atom in **5a**, we wondered if the cations could also be employed directly in proton-transfer reactions. Therefore, we studied the reaction of P_4 with a 3:2 mixture of **4a**[I] and KO*t*Bu.[39] Although **5a** still formed under these conditions,

the workup of the reaction mixture afforded a reduced yield of this product and a sizeable amount of recovered imidazolium salt. Thus, we conclude that the deprotonation of the imidazolium ions by a stoichiometric quantity of base is mandatory and that the carbene formed through deprotonation, not the imidazolium ion, is the active reagent in the formation of **5a**.

In addition to the resonances of P_4 and **5a**, the ^{31}P NMR spectra recorded during the reaction of **4a**[I] with P_4 and KO*t*Bu at –20 °C showed a characteristic signal pattern [AK_2MX spin system with A, K, M = ^{31}P, X = ^{1}H; $\delta^{31}P$ = 68.9 (A), –358.0 (K), –330.0 ppm (M); $\delta^{1}H$ = –4.3 ppm (X); $J_{A,K}$ = –194, $J_{A,M}$ = 12, $J_{K,M}$ = –244, $J_{A,X}$ = 16, $J_{K,X}$ = 128, $J_{M,X}$ = 3.6 Hz] attributable to the tetraphosphide anion **11** (Scheme 8).[40] The signals of **11** and P_4 persisted as long as a temperature of –20 °C was maintained but disappeared when the mixture was warmed to ambient temperature to give rise to complex, unidentified line patterns. As the anion **11** was reported to decay at room temperature to P-richer phosphides[40] and polyphosphides in general are known to equilibrate with each other or with P_4 under the assembly of new polyphosphorus frameworks,[41,42] we interpret the spectral changes as an indication that **11** and P_4 had reacted to yield higher polyphosphide(s) with as yet unknown molecular structures.[43]

Although **11** was originally obtained by the reduction of P_4 with Na/K naphthalenide,[40] tetraphosphabicyclo[1.1.0]butane anions are also discussed as the initial products of the activation of P_4 by nucleophiles.[42] We consider this pathway as the most likely explanation for the formation of **11** in the present case. Nevertheless, we can discuss two alternatives. One is the formation of **11** and other polyphosphides after the decay of one of the initial products of the carbene-activation of P_4, similar to the formation of $[(carbene)_2P]^+$ cations together with anionic species observed by Bertrand and co-workers.[14] The other is the direct nucleophilic activation of P_4 by KO*t*Bu. The formation of products attributed as phosphides in a binary reaction of both components was established independently (see Supporting Information). However, as the monitoring of a reaction of an in situ generated carbene/*t*BuOH mixture with P_4 indicated that the formation of observable amounts of soluble or insoluble phosphides[44] lagged behind that of **5a**, we assume that the second alternative is less plausible.

It should be noted that the observation of phosphide formation in reactions of P_4 with imidazolium salts and *t*BuOH establishes a parallel to the reported synthesis of **5d** from **4d**[Cl] and $(Me_3Si)_3P_7$ via an intermediate salt [NHC–H][$P_7(SiMe_3)_2$].[20] Even if the mechanism of this transformation is still unknown, in this case, it can be envisaged that **5d** may be formed by an alternative route that bypasses a direct carbene-activation of P_4. We consider this option less likely for the reactions studied here, as it would provide no forthright explanation for the observed formation of transient tetraphosphatrienes **10** in the synthesis of **5c**. However, as proton transfers or interconversion between polyphosphides and P_4 are reversible processes and, in principle, may occur in either direction, an analysis of the interplay of the individual reaction steps observed in the formation of **5** is exceedingly difficult. Thus, we are unable to give a detailed mechanistic explanation of this reaction.

Conclusions

We have demonstrated the one-step synthesis of the phosphaalkenes **5a**–**5d** with varying steric bulk and salts **6a**[X] and **6b**[X] (X = I, OTf) with bis(NHC)-stabilized phosphorus cations from P_4 in presence of an imidazolium salt and KO*t*Bu. Furthermore, we have established a safe and high-yielding procedure for the conversion of white or red phosphorus into the heptaphosphides Na_3P_7 and $(Me_3Si)_3P_7$. Although the latter was used previously only for the synthesis of N-arylated imidazoyl phosphinidenes and did not give access to *N*-alkyl derivatives, Na_3P_7 is a versatile precursor for the synthesis of both types of phosphaalkenes. This allows tuning of the reactivity by the steric demand and, thus, might open up new reaction pathways and applications.

At first glance, the conversion of elemental phosphorus into a mixture of species with formally lower (**5a** and **5b**) and higher (**6a** and **6b**) phosphorus oxidation states resembles the alkaline disproportionation of elemental phosphorus to give PH_3 and hypophosphorous acid. However, the finding that the formal disproportionation products are clearly generated through independent reaction channels and the observation of polyphosphorus species as coproducts indicate that this reaction proceeds by a different mechanism. Spectroscopic studies of low-temperature reactions suggest that phosphaalkenes **5** are formed through an initial carbene-activation of P_4 and subsequent trapping of the formed products by *t*BuOH, which arises as a byproduct of the carbene generation. Thus, the simultaneous reaction of P_4 with a carbene and a weak Brønsted acid, which may be considered a "frustrated Brønsted pair", might open new avenues for the formation of low-coordinate phosphorus species or P_4 activation, if the currently rather low atom economy is neglected. We are now exploring the use of a wider range of imidazolium precursors and attempting to optimize the reaction conditions to improve the atom economy.

Experimental Section

General Conditions: All manipulations were performed under dry argon in Schlenk apparatus or a glovebox. Solvents were dried by standard procedures. White phosphorus was washed with Et_2O and subsequently sublimed at 4×10^{-2} bar and 50 °C. The solution NMR spectra were recorded with Bruker Avance AV 400 or AV 250 instruments (^{1}H: 400.1/250.0 MHz, ^{13}C: 100.5/62.9 MHz, ^{31}P: 161.9/101.2 MHz). The chemical shifts are referenced to external tetramethylsilane (TMS; ^{1}H, ^{13}C) or 85 % H_3PO_4 (Ξ = 40.480747 MHz, ^{31}P). Coupling constants are given as absolute values. The solid-state NMR spectra were recorded with a Bruker Avance 400 spectrometer (^{13}C: 100.5 MHz, ^{31}P: 161.9 MHz) equipped with a 4 mm MAS probe. All experiments were performed under MAS with spinning speeds between 8 and 12 kHz and high-power ^{1}H decoupling during data acquisition. Cross-polarization (CP) was applied with a ramp-shaped contact pulse and mixing times of 5 (^{31}P) and 2.7 ms (^{13}C). The FTIR spectra were recorded with a Thermo Scientific Nicolet iS5 instrument equipped with an iD5 attenuated total reflectance (ATR) accessory. Elemental analyses were performed with an Elementar Micro Cube. The imidazolium salts **4a**[I], **4b**[I],[45] **4a**[Cl],[46] **4c**[Cl], **4d**[Cl],[47] **4e**[Cl] [48] and **4f**[Cl][49] were synthesized according to literature procedures. Melting points were determined with a Büchi B-545 melting point apparatus with samples in sealed

capillaries. 1,3-Dimethyl[D_1]imidazolium iodide and 1,3-[D_3]dimethylimidazolium chloride were prepared by analogy to the corresponding 1-butyl-3-methyl imidazolium tetrafluoroborates by H/D exchange in D_2O or D_2O/cat. NaOH.[38] Purification of the crude products was accomplished through a modified procedure, which is described in the Supporting Information. 1,3-[D_2]Dimethylimidazolium chloride was prepared by subjecting the D_3 derivative to H/D exchange in H_2O and analogous workup. The degree of deuteration was determined by ^{1}H NMR spectroscopy (see Supporting Information).

Compounds 5a/6a[X] from the Reaction of P_4 with 4a[I] and KO*t*Bu: A mixture of solid **4a**[I] (2.00 g, 8.93 mmol), KO*t*Bu (1.00 g, 8.93 mmol) and white phosphorus (552 mg, 4.46 mmol) was dispersed in THF (100 mL), and the resulting slurry was agitated by magnetic stirring. The liquid phase eventually adopted a yellow colour, and a red precipitate formed. Stirring was continued for 24 h. The solids were then separated by filtration through a sinter plate and washed with THF (2 × 25 mL). The filtrate was evaporated to dryness under reduced pressure. The remaining residue was dispersed in benzene (50 mL), and the dispersion was filtered. The new filtrate was again evaporated to dryness. The sublimation of the solid residue at 50 °C and 4×10^{-2} bar afforded **5a** (268 mg, 2.09 mmol, yield 23 % with respect to **4a**[I]) as a colourless solid (m.p. 85 °C). Single crystals suitable for an XRD study were obtained by recrystallization from benzene. The red solid remaining after the filtration of the original reaction mixture was extracted with CH_2Cl_2 (2 × 80 mL). The combined extracts were concentrated under reduced pressure to a total volume of 10 mL, and the resulting solution was stored at –15 °C. A crystalline, bright yellow precipitate formed and was collected by filtration to give **6a**[I] (836 mg, 2.39 mmol, yield 54 % with respect to **4a**[I]), m.p. >150 °C (dec.). The residue of the last filtration was dried under reduced pressure and characterized by CP/MAS ^{31}P and ^{13}C NMR spectroscopy (see Supporting Information).

1,3-Dimethyl-2-phosphanylidene-2,3-dihydro-1*H*-imidazole (5a): ^{1}H NMR ([D_8]THF, 250 MHz): δ = 6.69 (s, 2 H, HC=), 3.26 (d, $^4J_{P,H}$ = 0.9 Hz, 6 H, *N*CH_3), 1.68 (d, $^1J_{P,H}$ = 164 Hz, 1 H, PH) ppm. ^{1}H NMR (C_6D_6, 250 MHz): δ = 5.56 (d, $^4J_{P,H}$ = 0.5 Hz, =CH), 2.73 (d, $^4J_{P,H}$ = 1.0 Hz, 6 H, *N*CH_3), 2.38 (d, $^1J_{P,H}$ = 165 Hz, 1 H, PH) ppm. ^{31}P NMR ([D_8]THF, 101.2 MHz): δ = –155 (d, $^1J_{P,H}$ = 164 Hz) ppm. ^{31}P NMR (C_6D_6, 101.2 MHz): δ = –149.3 (d, $^1J_{P,H}$ = 165 Hz) ppm. ^{13}C{^{1}H} NMR ([D_8]THF, 62.9 MHz): δ = 178.0 (d, $^1J_{C,P}$ = 66 Hz, P=C), 118.0 (d, $^2J_{P,C}$ = 3.4 Hz, =CH), 34.6 (d, $^2J_{P,C}$ = 6.9 Hz, NCH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 62.9 MHz): δ = 176.0 (d, $^1J_{C,P}$ = 66 Hz, P=C), 116.0 (d, $^2J_{P,C}$ = 3.0 Hz, =CH), 33.5 (d, $^2J_{C,P}$ = 6.7 Hz, NCH_3) ppm. IR: $\tilde{\nu}$ = 3161 (s), 3127 (s), 3105 (s), 2311 (vs), 1483 (m), 1437 (m), 1391 (m), 1338 (m), 1233 (s), 1156 (s), 885 (m), 699 (vs), 646 (m), 628 (w) cm^{-1}. $C_5H_9N_2P$ (128.11): calcd. C 46.88, H 7.08, N 21.87; found C 46.80, H 7.09, N 21.80.

Bis[1,3-dimethyl-1*H*-imidazol-2(3*H*)-ylidene]phosphenium Iodide (6a[I]): ^{1}H NMR (CD_2Cl_2, 250 MHz): δ = 7.78 (s, 4 H, =CH), 3.55 (d, $^4J_{P,H}$ = 0.5 Hz, 12 H, NCH_3) ppm. ^{31}P NMR (CD_2Cl_2, 101.2 MHz): δ = –117.3 (s) ppm. ^{31}P CP/MAS NMR (161.9 MHz): δ = –119 ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 62.9 MHz): δ = 159.0 (d, $^1J_{C,P}$ = 77 Hz, P=C), 123.0 (d, $^2J_{C,P}$ = 2.8 Hz, =CH), 36.9 (d, $^2J_{C,P}$ = 7.0 Hz, NCH_3) ppm. IR: $\tilde{\nu}$ = 3138 (w), 3070 (m), 1662 [v(s)], 1565 (s), 1466 (w), 1437 (w), 1386 (m), 1238 (s), 1174 (m), 1147 (m), 1089 (vs), 904 (m), 760 (s), 740 (w), 656 (w), 619 (s) cm^{-1}. $C_{10}H_{16}IN_4P$ (350.14): calcd. C 34.30, H 4.61, N 16.00; found C 34.30, H 4.74, N 15.70.

Bis[1,3-dimethyl-1*H*-imidazol-2(3*H*)-ylidene]phosphenium Triflate (6a[OTf]): Trimethylsilyl triflate (0.40 mL, 489 mg, 2.20 mmol) was added to a solution of **6a**[I] (700 mg, 2.00 mmol) in THF (5 mL), and the mixture was stirred overnight. The solvent was removed under reduced pressure. The remaining bright yellow solid was suspended in CH_2Cl_2 (5 mL), and the colourless solid was removed by filtration. The filtrate was concentrated to a volume of 1 mL and stored at –15 °C to yield **6a**[OTf] (724 mg, 1.94 mmol, yield 97 %) as a bright yellow crystalline precipitate, m.p. >165 °C (dec.). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 7.19 (d, $^3J_{H,H}$ = 0.5 Hz, 4 H, =CH), 3.51 (s, 12 H, NCH_3) ppm. ^{31}P NMR (THF, 101.2 MHz): δ = –117.2 (s) ppm. ^{31}P NMR (CD_2Cl_2, 101.2 MHz): δ = –115.7 (s) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 62.9 MHz): δ = 159.9 (d, $^1J_{C,P}$ = 91 Hz, P=C), 123.2 (d, $^2J_{C,P}$ = 2.8 Hz, =CH), 121.5 (q, $^1J_{C,F}$ = 321 Hz, CF_3), 37.1 (d, $^2J_{C,P}$ = 7.1 Hz, NCH_3) ppm. IR: $\tilde{\nu}$ = 3121 (w), 3082 (m), 2923 (m), 1630 (w), 1563 (s), 1469 (m), 1379 (m), 1250 (s), 1228 (vs), 1148 (vs), 1029 (vs), 763 (m), 637 (vs) cm^{-1}. $C_{11}H_{16}F_3N_4O_3PS$ (372.30): calcd. C 35.49, H 4.33, N 15.05; found C 35.40, H 4.39, N 14.80.

Compounds 5b/6b[X] from the Reaction of P_4 with 4b[I]/KO*t*Bu: A mixture of solid **4a**[I] (401 mg, 1.59 mmol), KO*t*Bu (175 mg, 1.59 mmol) and white phosphorus (99 mg, 0.80 mmol) was dispersed in THF (16 mL), and the resulting slurry was agitated by magnetic stirring. The liquid phase eventually adopted a yellow colour, and a red precipitate formed. Stirring was continued for 24 h. The solids were then separated by filtration through a sinter plate and washed with THF (2 × 6 mL). The filtrate was evaporated to dryness under reduced pressure. The remaining residue was dispersed in benzene (50 mL), and the dispersion was filtered. The new filtrate was again evaporated to dryness. The sublimation of the solid residue at 95 °C and 4×10^{-2} bar afforded **5b** (64 mg, 0.41 mmol, yield 26 % with respect to **4b**[I]) as a colourless solid (m.p. 134 °C). The red solid remaining after the filtration of the original reaction mixture was extracted with CH_2Cl_2 (2 × 15 mL). The combined extracts were concentrated under reduced pressure to a total volume of 3 mL, and the resulting solution was stored at –15 °C. A bright yellow crystalline precipitate formed and was collected by filtration to give **6b**[I] (304 mg, 0.75 mmol, yield 47 % with respect to **4b**[I]); m.p. >140 °C (dec.).

1,2,3,4-Tetramethyl-2-phosphanylidene-2,3-dihydro-1*H*-imidazole (5b): ^{1}H NMR (C_6D_6, 250 MHz): δ = 2.83 (d, $^4J_{P,H}$ = 0.5 Hz, 6 H, NCH_3), 2.51 (d, $^1J_{P,H}$ = 165 Hz, 1 H, PH), 1.25 (s, 6 H, CH_3) ppm. ^{1}H NMR ([D_8]THF, 250 MHz): δ = 3.22 (d, $^4J_{P,H}$ = 0.6 Hz, 6 H, NCH_3), 2.03 (s, 6 H, CH_3), 1.71 (d, $^1J_{P,H}$ = 164 Hz, 1 H, PH) ppm. ^{31}P NMR (C_6D_6, 101.2 MHz): δ = –148.8 (d, $^1J_{P,H}$ = 165 Hz) ppm. ^{31}P NMR ([D_8]THF, 101.2 MHz): δ = –153.5 (d, $^1J_{P,H}$ = 164 Hz) ppm. ^{13}C{^{1}H} NMR ([D_8]THF, 62.9 MHz): δ = 174.7 (d, $^1J_{P,C}$ = 89 Hz, P=C), 120.7 (d, $^1J_{C,C}$ = 3.2 Hz, =C), 30.7 (s, NCH_3), 7.5 (s, CH_3) ppm. IR: $\tilde{\nu}$ = 2928 (w), 2295 (vs), 1664 (w), 1459 (w), 1433 (w), 1381 (vs), 1345 (vs), 1221 (m), 1164 (s), 1096 (m), 921 (m) cm^{-1}. $C_7H_{13}N_2P$ (156.17): C 53.84, H 8.39, N 17.94; found C 53.44, H 8.36, N 17.75.

Bis[1,2,3,4-tetramethyl-1*H*-imidazol-2(3*H*)-ylidene]phosphenium Iodide (6b[I]): ^{1}H NMR (CD_2Cl_2, 250 MHz): δ = 3.47 (s, 12 H, CCH_3), 2.25 (s, 12 H, NCH_3) ppm. ^{31}P NMR (CD_2Cl_2, 101.2 MHz): δ = –113.0 (s) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 62.9 MHz): δ = 159.0 (d, $^1J_{C,P}$ = 77 Hz, P=C), 126.8 (s, =C), 34.4 (d, $^2J_{C,P}$ = 7.9 Hz, NCH_3), 9.92 (s, CCH_3) ppm.

Reactions of P_4 with 4c[Cl]/4d[Cl] and KO*t*Bu: A mixture of solid imidazolium salt (**4c**[Cl]: 500 mg, 1.47 mmol; **4d**[Cl]: 625 mg, 1.47 mmol), KO*t*Bu (165 mg, 1.47 mmol) and white phosphorus (91 mg, 0.73 mmol) was dispersed in THF (20 mL), and the resulting slurry was agitated by magnetic stirring. The liquid phase eventually turned violet, and a dark precipitate formed. Stirring was continued for 48 h. Compound **5d** was characterized by ^{31}P NMR spectroscopic analysis of the reaction mixture. For the isolation of **5c**, the solids were separated by filtration through a sinter plate. The filtrate

was concentrated to ca. 5 mL and stored at r.t. to produce **5c** (123 mg, 0.37 mmol, yield 25 % with respect to **4c**[Cl]) as a crystalline precipitate. Further purification was performed by sublimation at 50 °C and 4×10^{-2} bar to afford the product (98 mg,0.29 mmol, yield 20 % with respect to **4c**[Cl]).

1,3-Dimesityl-2-phosphanylidene-2,3-dihydro-1*H*-imidazole (5c): ^{1}H NMR (C_6D_6, 250 MHz): δ = 6.76 (s, 4 H, *m*-CH), 5.90 (s, 2 H, =CH), 2.21 (s, 12 H, *o*-CH_3), 2.08 (s, 6 H, *p*-CH_3), 1.78 (d, $^1J_{P,H}$ = 165 Hz, PH) ppm. ^{1}H NMR ([D$_8$]THF, 250 MHz): δ = 6.98 (s, 4 H, *m*-CH), 6.82 (s, 2 H, =CH), 2.31 (s, 12 H, *p*-CH_3), 2.14 (s, 6 H, *o*-CH_3), 1.26 (d, $^1J_{P,H}$ = 164 Hz, PH) ppm. ^{31}P NMR (C_6D_6, 101.2 MHz): δ = –147.3 (d, $^1J_{P,H}$ = 165 Hz) ppm. ^{31}P NMR ([D$_8$]THF, 101.2 MHz): δ = –149.6 (d, $^1J_{P,H}$ = 164 Hz) ppm. ^{13}C NMR (C_6D_6, 62.9 MHz): δ = 129.3 (s, =CH), 127.8 (s, *m*-CH), 20.6 (s, *p*-CH_3), 17.8 (s, *o*-CH_3) ppm. ^{13}C NMR ([D$_8$]THF, 62.9 MHz): δ = 180.0 (d, $^1J_{P,C}$ = 93.5 Hz, P=C), 129.0 (s, *m*-CH), 118.0 (s, =CH), 20.3 (s, *o*-CH_3), 17.3 (s, *p*-CH_3) ppm.

1,3-Bis(2,6-diisopropylphenyl)-2-phosphanylidene-2,3-dihydro-1*H*-imidazole (5d): ^{31}P NMR (C_6D_6, 101.2 MHz): δ = –135.0 (d, $^1J_{P,H}$ = 165 Hz) ppm.

[(Na_3P_7)(DME)$_x$]: A suspension of white phosphorus (10.0 g, 80.7 mmol, 1.75 equiv.), freshly cut sodium (3.17 g, 138 mmol, 3 equiv.) and naphthalene (400 mg, 3.13 mmol, 0.07 equiv.) in a mixture of THF (50 mL) and DME (50 mL) was stirred for 3 d at 20 °C until a bright orange suspension formed. The suspension was concentrated, and the yellow precipitate was collected by filtration and washed thoroughly with *n*-hexane (10 × 10 mL) to remove the naphthalene. Drying at reduced pressure and 20 °C for 6 h yielded trisodium heptaphosphide as an orange powder, which was soluble in THF. Further drying at reduced pressure and 60 °C for 3 d yielded an insoluble orange-red powder. The phosphorus content was determined photometrically to be 72.5 %, which corresponds to a residual DME content of $x \approx 0.12$ (13.5 g, 45.5 mmol, yield 99 %).

Alternative synthesis from red phosphorus: Red phosphorus (40.0 g, 1.29 mol, 7 equiv.), freshly cut sodium (12.7 g, 0.550 mol, 3 equiv.) and naphthalene (4.95 g, 38.7 mmol, 0.21 equiv.) were suspended in a mixture of THF (50 mL) and DME (50 mL). The dark green suspension was stirred at 20 °C for 18 h until all of the sodium was consumed. The resulting black suspension was heated under reflux for 24 h until a bright orange suspension formed. The insoluble yellow precipitate was collected by filtration, thoroughly washed with *n*-hexane (6 × 40 mL) to remove the naphthalene and dried at reduced pressure and 60 °C for 3 d (54.0 g, 0.182 mol, yield 99 %).

^{31}P{^{1}H}NMR (THF, 101 MHz): δ = –119.0 (br s) ppm. [(Na_3P_7)-($C_4H_{10}O_2$)$_{0.12}$]: calcd. C 1.9, H 0.4, N 0; found C 2.0, H 0.6, N 0.1.

(Me_3Si)$_3P_7$ from [(Na_3P_7)(DME)$_x$]: To a stirred suspension of [(Na_3P_7)(DME)$_{0.12}$] (1.43 g, 4.81 mmol, 1 equiv.) in toluene (10 mL) was added trimethylsilyl chloride (2.3 mL, 18 mmol, 1.25 equiv.) at –80 °C over 15 min. The suspension was stirred and slowly warmed to 20 °C over 3 h. The pale precipitate was removed from the yellow solution by filtration through Celite. The removal of the solvent under reduced pressure and recrystallization from toluene at –30 °C yielded tris(trimethylsilyl) heptaphosphide as a pale yellow powder (1.96 g, 4.49 mmol, yield 94 %). The elemental analysis data and the ^{1}H, ^{13}C and ^{31}P NMR spectra were identical to the previously reported data.[22]

***N*-Alkylated Imidazoyl Phosphinidenes from [(Na_3P_7)(DME)$_x$]:** The corresponding imidazolium salt (**4a**[Cl]: 497 mg; **4e**[Cl]: 708 mg; 3.75 mmol, 3 equiv.) and [(Na_3P_7)(DME)$_x$] (500 mg, 1.68 mmol, 1.35 equiv.) were suspended in THF (10 mL), and the mixture was heated under reflux for 16 h. The resulting orange suspension was filtered through a G3 glass frit and washed with THF (3 × 3 mL). The combined filtrates were evaporated to dryness, and the residue was extracted with toluene (5 × 3 mL). The combined extracts were filtered through Celite, and the solvent was removed under reduced pressure. The yellow residue was recrystallized from toluene at –30 °C to yield the phosphaalkenes **5a** and **5e** as pale yellow crystalline solids (**5a**: 340 mg, 2.61 mmol, 70 %; **5e**: 456 mg, 2.48 mmol, 66 %).

1,3-Diisopropyl-2-phosphanylidene-2,3-dihydro-1*H*-imidazole (5e): M.p. 132–133 °C. ^{1}H NMR (300 MHz, C_6D_6): δ = 6.12 (s, 2 H, *H*C=C*H*), 4.49 [sept d, $^3J_{H,H}$ = 6.7, $^4J_{P,H}$ = 2.7 Hz, 2 H, C*H*-(CH_3)$_2$], 2.63 (d, $^1J_{P,H}$ = 165.9 Hz, 1 H, P–*H*), 0.95 [d, $^3J_{H,H}$ = 6.7 Hz, 12 H, CH(*CH*$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ = 173.7 (d, $^1J_{P,C}$ = 92.9 Hz, *C*=P), 113.2 (s, HC=*C*H), 48.8 [s, *C*H(CH$_3$)$_2$], 21.2 [s, CH(CH_3)$_2$] ppm. ^{31}P{^{1}H} NMR (THF, 121 MHz): δ = –149.9 (s) ppm. ^{31}P NMR (THF, 121 MHz): δ = –149.9 (d, $^1J_{P,H}$ = 166.1 Hz) ppm. $C_9H_{17}N_2P$ (184.22): calcd. C 58.7, H 9.3, N 15.2; found C 58.4, H 9.5, N 14.9.

N-Arylated Imidazoyl Phosphinidenes from [(Na_3P_7)(DME)$_x$]: The corresponding imidazolium salt (**4c**[Cl]: 1.28 g; **4d**[Cl]: 1.59 g; **4f**[Cl]: 1.60 g; 3.75 mmol; 3 equiv.) and Na_3P_7 (500 mg, 1.75 mmol, 1.35 equiv.) were suspended in THF (10 mL), and the suspension was stirred at 20 °C for 16 h. The brown-black precipitate was removed from the red solution by filtration through a G3 glass frit and washed with THF (3 × 3 mL). Further workup was performed as described above for the N-alkylated species (**5c**: 760 mg, 2.25 mmol, 60 %; **5d**: 1.26 g, 3.00 mmol, 80 %; **5f**: 1.04 g, 2.46 mmol, 66 %). The elemental analysis data as well as the ^{1}H, ^{13}C and ^{31}P NMR spectra correspond to the data given above for **5c** and the previously reported data for **5d**[20] and **5f**.[21]

Crystal Structure Determinations: X-ray diffraction studies of **5a**–**5c**, **6a**[I], **6b**[I] and **6a**[OTf] were performed with a Bruker diffractometer equipped with a Kappa APEX II Duo CCD detector and a KRYO-FLEX cooling device with Mo-K_α radiation (λ = 0.71073 Å) at T = 100 K. The structures were solved by direct methods (SHELXS-97[50]) and refined with a full-matrix least-squares scheme on F^2 (SHELXL-2014 and SHELXL-97).[50] Semiempirical absorption corrections were applied for all structures. Non-hydrogen atoms were refined anisotropically, and H atoms were refined isotropically with a riding model [H(P) free]. Crystalline **5b** contains two crystallographically independent molecules. One of these resides at a special position with crystallographic C_2 symmetry and features a H(P) atom that is disordered over two positions. The H1 atom in **5c** is disordered over two positions. Owing to the low quality of the crystal, the data of **6a**[I] is included in the Supporting Information but was not deposited at the CCDC.

CCDC-1414812 (for **5a**), -1422252 (for **5b**), -1414813 (for **5c**), -1414811 (for **6a**[OTf]) and –1422307 (for **6b**[I]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Compound 5a: Colourless crystals, $C_5H_9N_2P$, M: 128.11 g mol^{-1}, crystal size: 0.36 × 0.16 × 0.11 mm, monoclinic, space group $P2_1/n$, a = 6.7979(19) Å, b = 11.661(3) Å, c = 8.641(2) Å, β = 91.021(15)°, V = 684.8(3) A^3, Z = 4, ρ(calcd.) = 1.243 Mg m^3, F(000) = 272, θ_{max} = 28.34°, μ = 0.299 mm^{-1}, 5924 reflections measured, 1685 unique reflections [R_{int} = 0.047] for structure solution and refinement with 78 parameters, $R1$ = 0.065 [for 1156 reflections with $I > 2\sigma(I)$], $wR2$ = 0.189, largest diff. peak and hole: 1.221 and –0.612 e Å^{-3}.

Compound 5b: Colourless crystals, $C_7H_{13}N_2P$, M: 156.16 g mol^{-1}, crystal size: 0.52 × 0.40 × 0.34 mm, monoclinic, space group $C2/c$, a = 22.265(2) Å, b = 8.6445(6) Å, c = 14.0303(12) Å, β = 107.512(5)°,

V = 2575.3(4) Å^3, Z = 12, ρ(calcd.) = 1.208 Mg m^3, F(000) = 1008, θ_{max} = 30.56°, μ = 0.251 mm^{-1}, 16120 reflections measured, 3950 unique reflections [R_{int} = 0.026] for structure solution and refinement with 150 parameters and one restraint, $R1$ = 0.040 [for 2846 reflections with $I > 2\sigma(I)$], $wR2$ = 0.114, largest diff. peak and hole: 0.435 and –0.292 e Å^{-3}.

Compound 5c: Yellow crystals, $C_{21}H_{25}N_2P$, M: 336.40 g mol^{-1}, crystal size: 0.23 × 0.21 × 0.10 mm, monoclinic, space group $P2_1/n$, a = 8.2558(9) Å, b = 14.6092(17) Å, c = 16.1057(14) Å, β = 102.010(4)°, V = 1900.0(3) Å^3, Z = 4, ρ(calcd.) = 1.176 Mg m^3, F(000) = 720, θ_{max} = 27.48°, μ = 0.149 mm^{-1}, 17209 reflections measured, 4341 unique reflections [R_{int} = 0.074] for structure solution and refinement with 230 parameters, $R1$ = 0.056 [for 2439 reflections with $I > 2\sigma(I)$], $wR2$ = 0.134, largest diff. peak and hole: 0.272 and –0.321 e Å^{-3}.

Compound 6a[OTf]: Bright yellow crystals, $C_{10}H_{16}N_4P{\cdot}CF_3O_3S$, M: 372.31 g mol^{-1}, crystal size: 0.36 × 0.30 × 0.24 mm, triclinic, space group $P\bar{1}$, a = 11.6579(9) Å, b = 12.3283(9) Å, c = 12.9947(10) Å, α = 116.937(3)°, β = 102.470(4)°, γ = 91.388(4)°, V = 1609.7(2) Å^3, Z = 4, ρ(calcd.) = 1.536 Mg m^3, F(000) = 768, θ_{max} = 27.48°, μ = 0.350 mm^{-1}, 65509 reflections measured, 7368 unique reflections [R_{int} = 0.021] for structure solution and refinement with 415 parameters, $R1$ = 0.028 [for 6673 reflections with $I > 2\sigma(I)$], $wR2$ = 0.074, largest diff. peak and hole: 0.967 and –0.330 e Å^{-3}.

Compound 6b[I]: Bright yellow crystals, $C_{14}H_{24}IN_4P$, M: 406.24 g mol^{-1}, crystal size: 0.26 × 0.22 × 0.20 mm, monoclinic, space group $P2_1/n$, a = 11.7734(5) Å, b = 11.4627(5) Å, c = 13.1048(6) Å, β = 90.714(2)°, V = 1768.42(13) Å^3, Z = 4, ρ(calcd.) = 1.526 Mg m^3, F(000) = 816, θ_{max} = 36.35°, μ = 1.899 mm^{-1}, 68773 reflections measured, 8502 unique reflections [R_{int} = 0.042] for structure solution and refinement with 189 parameters, $R1$ = 0.029 [for $I > 2\sigma(I)$], $wR2$ = 0.061, largest diff. peak and hole: 2.067 and –1.231 e Å^{-3}.

Supporting Information (see footnote on the first page of this article): Synthetic procedures for deuterated 1,3-dimethylimidazolium salts; ^{31}P NMR spectra of reaction mixtures of **4a**/KO*t*Bu/P_4 and **4c**/KO*t*Bu/P_4 obtained under different reaction conditions; CP/MAS NMR spectra of the solid residue of a reaction of **4a**/KO*t*Bu/P_4 before and after extraction with CH_2Cl_2; representations of the molecular structures of **5b**[I], **5c**[I] and **6b**[I], and the preliminary molecular structure of **6a**[I].

Acknowledgments

The authors thank Dr. W. Frey (Institute of Organic Chemistry, University of Stuttgart, Germany) for the collection of X-ray data sets. Furthermore, the University of Stuttgart, Germany, ETH Zürich, Switzerland, and the European Union (Marie Curie ITN SusPhos, grant agreement number 317404) are acknowledged for financial support.

Keywords: Carbenes · Phosphorus · Phosphaalkenes · P–P activation · Nitrogen heterocycles

[1] W. F. Dahsent, *Nonexistent Compounds*, Marcel Dekker, New York, **1965**.
[2] For overviews, see: a) P. P. Power, *Chem. Rev.* **1999**, *99*, 3463–3503; b) R. C. Fischer, P. P. Power, *Chem. Rev.* **2010**, *110*, 3877–3923.
[3] For selected reviews, see: a) L. Weber, *Angew. Chem. Int. Ed.* **2002**, *41*, 563; *Angew. Chem.* **2002**, *114*, 583; b) P. Le Floch, *Coord. Chem. Rev.* **2006**, *250*, 627; c) G. Fu, *Acc. Chem. Res.* **2006**, *39*, 853; d) C. Müller, D. Vogt, *Dalton Trans.* **2007**, 5505; e) C. Ganter, in: *Phosphorus Ligands, in: Asymmetric Catalysis* (Ed.: A. Börner), Wiley-VCH, Weinheim, Germany, **2008**; p. 393–406; f) J. I. Bates, J. Dugal-Tessier, D. P. Gates, *Dalton Trans.* **2010**, *39*, 3151; g) M. Nicolas, G. C. Fu, in: *Chiral Ferrocenes in Asymmetric Catalysis* (Eds.: L.-X. Dai, X.-L. Hou), Wiley-VCH, Weinheim, Germany, **2010**, ch. 11, p. 307–335.
[4] For selected reviews, see: a) M. Hissler, P. W. Dyer, R. Réau, in: *Topics in Current Chemistry*, vol. 250 (Ed.: J.-P. Majoral), Springer, Berlin, **2005**, p. 127–163; b) P. W. Dyer, R. Réau, in: *Functional Organic Materials: Syntheses, Strategies, and Applications* (Eds.: T. J. J. Müller, U. H. F. Bunz), Wiley-VCH, Weinheim, Germany, **2007**, p. 119–178; c) P. W. Siu, D. P. Gates, in: *Conjugated Polymer Synthesis: Methods and Reactions* (Ed.: Y. Chujo), Wiley-VCH, Weinheim, Germany, **2010**, p. 215–227; d) J. D. Protasiewicz, in: *Comprehensive Inorganic Chemistry II*, vol. 1 (Eds.: J. Reedijk, K. Poeppelmeier), Elsevier, Amsterdam, **2013**, p. 325–348.
[5] P. P. Power, *J. Organomet. Chem.* **2004**, *689*, 3904.
[6] a) K. Dimroth, P. Hoffmann, *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 384; *Angew. Chem.* **1964**, *76*, 433; b) K. Dimroth, *Top. Curr. Chem.* **1973**, *38*, 1.
[7] D. Schmid, S. Loscher, D. Gudat, D. Bubrin, I. Hartenbach, Th. Schleid, Z. Benkö, L. Nyulászi, *Chem. Commun.* **2009**, 830–832.
[8] G. Becker, *Z. Anorg. Allg. Chem.* **1976**, *423*, 242.
[9] K. Issleib, E. Leißring, M. Riemer, H. Oehme, *Z. Chem.* **1983**, *23*, 99–100.
[10] In a few special cases, there is precedent for the direct access of multiply bonded species from elemental phosphorus, for example, P_5^-, see: a) M. Baudler, D. Düster, D. Ouzounis, *Z. Anorg. Allg. Chem.* **1987**, *544*, 47; b) M. Baudler, S. Akpapoglou, D. Ouzounis, F. Wasgestian, B. Meinigke, H. Budzikiewicz, H. Münster, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 280–281; *Angew. Chem.* **1988**, *100*, 288.
[11] J. D. Masuda, W. W. Schoeller, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2007**, *46*, 7052–7055; *Angew. Chem.* **2007**, *119*, 7182–7185.
[12] J. D. Masuda, W. W. Schoeller, B. Donnadieu, G. Bertrand, *J. Am. Chem. Soc.* **2007**, *129*, 14180–14181.
[13] O. Back, G. Kuchenbeiser, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2009**, *48*, 5530–5533; *Angew. Chem.* **2009**, *121*, 5638.
[14] C. D. Martin, C. M. Weinstein, C. E. Moore, A. L. Rheingold, G. Bertrand, *Chem. Commun.* **2013**, *49*, 4486–4488.
[15] For a review, see: D. Martin, M. Soleilhavoup, G. Bertrand, *Chem. Sci.* **2011**, *2*, 389–399.
[16] a) H. J. Schönherr, H. W. Wanzlick, *Chem. Ber.* **1970**, *103*, 1037–1046; b) N. I. Korotkikh, G. F. Rayenko, O. P. Shvaika, T. M. Pekhtereva, A. H. Cowley, J. N. Jones, C. L. B. MacDonald, *J. Org. Chem.* **2003**, *68*, 5762–5765; c) W. Zuo, P. Braunstein, *Dalton Trans.* **2012**, *41*, 636–643; d) P. K. Majhi, S. Sauerbrey, G. Schnakenburg, A. J. Arduengo, R. Streubel, *Inorg. Chem.* **2012**, *51*, 10408–10416.
[17] B. D. Ellis, C. A. Dyker, A. Decken, C. L. B. Macdonald, *Chem. Commun.* **2005**, 1965–1967.
[18] B. D. Ellis, C. L. B. Macdonald, *Coord. Chem. Rev.* **2007**, *251*, 936–973.
[19] a) K. Hansen, T. Szilvási, B. Blom, S. Inoue, J. Epping, M. Driess, *J. Am. Chem. Soc.* **2013**, *135*, 11795–11798.
[20] A. M. Tondreau, Z. Benkö, J. R. Harmer, H. Grützmacher, *Chem. Sci.* **2014**, *5*, 1545–1554.
[21] M. Bispinghoff, A. M. Tondreau, H. Grützmacher, C. A. Faradji, P. G. Pringle, *Dalton Trans.* **2015**, DOI: 10.1039/C5DT01741F.
[22] H. Schmidbaur, A. Bauer, *Phosphorus Sulfur Silicon Relat. Elem.* **1995**, *102*, 217–219.
[23] O. Back, M. Henry-Ellinger, C. D. Martin, D. Martin, G. Bertrand, *Angew. Chem. Int. Ed.* **2013**, *52*, 2939–2943; *Angew. Chem.* **2013**, *125*, 3011.
[24] A. Doddi, D. Bockfeld, T. Bannenberg, P. G. Jones, M. Tamm, *Angew. Chem. Int. Ed.* **2014**, *53*, 13568–13572; *Angew. Chem.* **2014**, *126*, 13786–13790.
[25] a) J. Schmedt auf der Günne, S. Kaczmarek, L. v. Wüllen, H. Eckert, D. Paschke, A. J. Foecker, W. Jeitschko, *J. Solid State Chem.* **1999**, *147*, 341; b) K. Eichele, R. E. Wasylishen, J. F. Corrigan, N. J. Taylor, A. J. Carty, K. W. Feindel, G. M. Bernard, *J. Am. Chem. Soc.* **2002**, *124*, 1541; c) A. Pfitzner, M. F. Bräu, J. Zweck, G. Brunklaus, H. Eckert, *Angew. Chem. Int. Ed.* **2004**, *43*, 4228; *Angew. Chem.* **2004**, *116*, 4324; d) M. Scheer, L. J. Gregoriades, M. Zabel, M. Sierka, L. Zhang, H. Eckert, *Eur. J. Inorg. Chem.* **2007**, 2775; e) T. Wiegand, H. Eckert, S. Grimme, D. Hoppe, M. Ruck, *Chem. Eur. J.* **2011**, *17*, 8739–8748.
[26] A single-crystal XRD study was also performed on **6a**[I]. Although the structure could be solved, satisfactory refinement remained unfeasible

owing to the low quality of the crystal. The preliminary results included in the Supporting Information confirm the constitutional assignment and reveal similar metrical parameters of the cation to those in **6a**[OTf].

[27] Y. Wang, Y. Xie, M. Y. Abraham, R. J. Gilliard Jr., P. Wei, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson, *Organometallics* **2010**, *29*, 4778–4780.

[28] L. Weber, *Eur. J. Inorg. Chem.* **2000**, 2425–2441.

[29] For **6a**[I], the angles differ further: 28.8(7) and 52.6(6)°.

[30] G. Frison, A. Sevin, *J. Organomet. Chem.* **2002**, *643–644*, 105–111.

[31] Z. Kelemen, R. Streubel, L. Nyulászi, *RSC Adv.* **2015**, *5*, 41795–41802.

[32] Attempts to reduce the amount of P_4 led to a decrease of the yield of **5a** and gave solutions that still contained unreacted carbene, which suggests that an initial P_4/NHC molar ratio of 1:2 is needed to ensure the complete consumption of the imidazolium salt.

[33] Spectral simulation of the signals of the minor component at δ = 328.4 and 50.8 ppm was prevented by the insufficient signal-to-noise (S/N) ratio. On the basis of the observed chemical shifts, we assign the major component as the *E*-isomer and the minor one as the *Z*-isomer.

[34] In this case, deprotonation yields H_2 as a byproduct, which evolves from the reaction mixture. Further reaction with P_4 gave only intractable insoluble phosphorus compounds and was not pursued further.

[35] The presence of water may at first glance seem incompatible with the proposed reaction, but NHCs may coexist with small amounts of H_2O, in: organic solvents (see ref.[37]), and we have also verified the stability of **6a** under such conditions.

[36] Similarly, the formation of products with P–D substituents was promoted when D_2O was added to the reaction mixture; see Supporting Information.

[37] O. Hollóczki, P. Terleczky, D. Szieberth, G. Mourgas, D. Gudat, L. Nyulászi, *J. Am. Chem. Soc.* **2011**, *133*, 780–789.

[38] R. Giernoth, D. Bankmann, *Eur. J. Org. Chem.* **2008**, 2881–2886.

[39] By using the notation [NHC–H^+] for an imidazolium salt, the formation of a mixture of **5a** and **6a** may be described formally by the following overall equation: 3[NHC–H^+]I^- + 1/2P_4 + 2KO*t*Bu → NHC=PH + [$(NHC)_2P^+$]I^- + 2*t*BuOH + 2KI. Thus, the formation of **5a** does not formally require a further stoichiometric amount of base beyond the two equivalents needed for the generation of [$(NHC)_2P^+$]I^- (**6a**).

[40] M. Baudler, C. Adamek, S. Opiela, H. Budzikiewicz, D. Ouzounis, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1059–1061; *Angew. Chem.* **1988**, *100*, 1110–1111.

[41] M. Baudler, K. Glinka, *Chem. Rev.* **1993**, *93*, 1623–1667.

[42] M. Scheer, G. Balázs, A. Seitz, *Chem. Rev.* **2010**, *110*, 4236–4256.

[43] For a specific reaction of an anionic tetraphosphabicyclo[1.1.0]-butane derivative with P_4 to give an octaphosphide anion, see: W. T. K. Chan, F. García, A. D. Hopkins, L. C. Martin, M. McPartlin, D. S. Wright, *Angew. Chem. Int. Ed.* **2007**, *46*, 3084–3086; *Angew. Chem.* **2007**, *119*, 3144.

[44] The formation of solid phosphides was recognized through the reddish colour of the formed precipitate.

[45] D. J. Williams, M. R. Fawcett-Brown, R. R. Raye, D. Van Derveer, Y. T. Pang, R. L. Jones, K. L. Bergbauer, *Heteroat. Chem.* **1993**, *4*, 409–414.

[46] M. Smiglak, J. D. Holbrey, S. T. Griffin, W. M. Reichert, R. P. Swatloski, A. R. Katritzky, H. Yang, D. Zhang, K. Kirichenko, R. D. Rogers, *Green Chem.* **2007**, *9*, 90–98.

[47] L. Hintermann, *Beilstein J. Org. Chem.* **2007**, *3*, 1–5.

[48] T. Schaub, U. Radius, in: *Inorganic Syntheses*, vol. 35 (Ed.: T. B. Rauchfuss), John Wiley & Sons, Hoboken, **2010**, p. 78–79.

[49] K. M. Kuhn, R. H. Grubbs, *Org. Lett.* **2008**, *10*, 2075–2077.

[50] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

Received: September 7, 2015
Published Online: October 22, 2015

