Synthesis of 1,3,5,2λ^5-Triazaphosphinines by Intramolecular Cyclisation of (*N*-Cyanophosphorimidoyl)guanidines and Diguanidinophosphonium Chlorides

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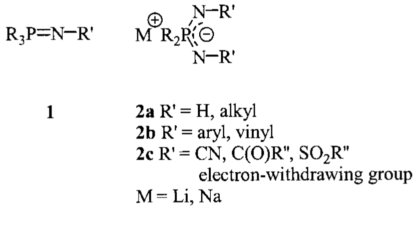
Dedicated to Professor Reinhard Schmutzler on the occasion of his 70th birthday

Keywords: Azides / Guanidines / P heterocycles / Phosphorus ylides

The sodium phosphonium diylide $Na[Ph_2P(NCN)_2]$ (**3**) – the first example of a stabilised phosphonium diylide – was synthesised by treatment of sodium diphenylphosphide with 2 equiv. of cyanic azide. Compound **3** reacted with alkyl- and arylammonium salts $[RR'NH_2]Cl$ {R = $PhCH_2$, *t*Bu, Ph; R′ = H; RR′ = $-[(CH_2)_2O(CH_2)_2]-$}. Depending on the molar ratios (1:1 or 1:2), (*N*-cyano-*P*,*P*-diphenylphosphorimidoyl)guanidines $Ph_2P(NCN)N{=}C(NH_2)NRR'$ (**8**) or diguanidinodiphenylphosphonium chlorides $[Ph_2P\{N{=}C(NH_2)NRR'\}_2]Cl$ (**10**) were formed. When molten, compounds **8** yielded new cyclic 1,3,5,2λ^5-triazaphosphinines **11**. The fusion of compound **10** allowed the formation of the same 1,3,5,2λ^5-triazaphosphinines **11**, along with the formation of NH_4Cl or $[PhNH_3]Cl$. A crystal structure analysis of 4-amino-6-morpholino-2,2-diphenyl-1,3,5,2λ^5-triazaphosphinine (**11a**) revealed an almost planar six-membered ring for the 1,3,5,2λ^5-triazaphosphinine template.

Introduction

Phosphonium ylides and diylides represent a well-characterised and growing group of compounds known as valuable and versatile reagents in organic synthesis.[1] Homologous nitrogen compounds − azaylides **1** and diazadiylides **2** − have also been described (Scheme 1).[2−4] Depending on their substituents R′ (Scheme 1), the diazadiylides can variously be non-stabilised (R′ = H, alkyl: **2a**), semi-stabilised (R′ = aryl, vinyl: **2b**) or stabilised [R′ = CN, RC(O), RSO_2: **2c**] species.[5,6] While the first compound of the non-stabilised type, $Li[tBu_2P(NH)_2]$, was first synthesised in 1969,[7] synthetic strategies for the preparation of stabilised diazadiylides have appeared only recently.[5,6]



Scheme 1. Phosphonium aza- and diazadiylides

Generally, non- and semi-stabilised diazadiylides can be prepared by lithiation of diaminophosphonium salts[2,3,8] However, this synthetic route failed for the preparation of stabilised diazadiylides **2c**. In the literature, series of cyanamidophosphates such as $Na_3[PSO_{3-n}(NCN)_n]$ (n = 1−3), or the phosphinates and phosphonates analogues, like $Na[Ph_2P(O)NCN]$ or $Na_2[PhP(O)(NCN)_2]$, are described;[9−11] therefore the synthesis of $M[Ph_2P(NCN)_2]$ (**3**) as the first stabilised diazadiylide appeared promising.

With regard to their potential applications, special diazadiylides usually serve as chelating ligands in coordination chemistry,[12] while the first examples of their applications as organic synthesis tools were described recently. They can be used, for instance, as precursors of primary and secondary amines[3] and have also afforded a new approach towards ketenimines $Ph_2C{=}C{=}NR$ [R = alkyl, Ph, C(O)Ph] under very mild conditions.[13] We now report the synthesis of sodium phosphonium diylide **3** and its reactivity towards substituted amine hydrochlorides $[RR'NH_2]Cl$ {R = $PhCH_2$, *t*Bu, Ph; R′ = H; RR′ = $-[(CH_2)_2O(CH_2)_2]-$} to afford novel (phosphorimidoyl)-

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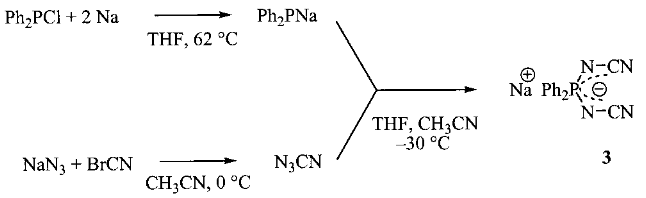
guanidines, which, when molten, underwent intramolecular cyclisation to yield 1,3,5,2λ^5-triazaphosphinines.

Results and Discussion

Synthesis of Sodium Phosphonium Diylides

The reactions between dibromodiphenylphosphonium bromide and amines represent a facile, efficient and versatile synthetic route to direct precursors of non- or semistabilised diazaylides, developed in our group.[3] This reaction did not proceed, however, in the presence of the less nucleophilic amides RC(O)NH$_2$ in place of substituted amines. On the other hand, the oxidation of phosphorus(III) compounds with azides (Staudinger reaction[2]), such as cyanic azide, is a very clean method by which to introduce an imide function.[10,14] Treatment of phosphanes or phosphites with N$_3$CN, for instance, yields the corresponding monoylides R$_3$PNCN or (RO)$_3$PNCN in high yields under mild conditions.

A new variant of the Staudinger reaction in which sodium diphenylphosphide reacts with 2 equiv. of cyanic azide[6] has proved suitable for the synthesis of Na[Ph$_2$P(NCN)$_2$] (**3**), the first example of a stabilised diazadiylide. To the best of our knowledge this is the first example of a Staudinger reaction involving a phosphide. Under an inert gas, a solution of N$_3$CN in acetonitrile was added at −30 °C to NaPPh$_2$ in absolute THF. The reaction was monitored by collection of the liberated nitrogen. After recrystallisation, **3** could be isolated in 80% yield (Scheme 2).



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Scheme 2. Synthesis of sodium phosphonium diylide **3**

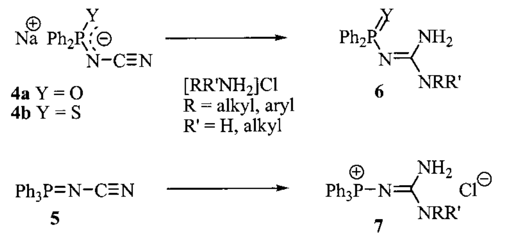
Compound **3** is a member of the homologous series [Ph$_2$PY$_{2-n}$(NCN)$_n$]$^-$ (Y = O, S; *n* = 1, 2).[10] In the ^{13}C NMR spectra, the NCN carbon resonances shifted to lower fields in the order **3**, **4a**, **4b**, because of the ability of the cyanamido group to accept a greater part of the ionic charge than one chalcogen atom in mixed chalcogeno-cyanimino compounds (Table 1). For the same reason, we also observed a shift of the ν$_{as}$(NCN) vibrations to lower wave numbers in the IR spectra.

Table 1. Selected spectroscopic data of **3**, **4a** and **4b**

	δ(^{13}C) [ppm]	ν$_{as}$(NCN) [cm^{-1}]	Ref.
Na[Ph$_2$P(NCN)$_2$] (**3**)	119.3	2190 vs, 2140 vs	
Na[Ph$_2$P(O)NCN] (**4a**)	121.7	2190 vs	[9]
Na[Ph$_2$P(S)NCN] (**4b**)	130.5	2145 vs	[9]

Reactivity of the Sodium Phosphonium Diylides

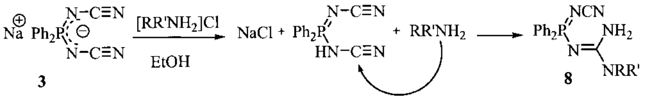
We had previously reported that the sodium phosphinates Na[Ph$_2$P(Y)NCN] [Y = O (**4a**), S (**4b**)] and triphenylphosphoranylidenecyanamide (Ph$_3$PNCN, **5**) reacted with alkylamine or arylamine hydrochlorides to give the corresponding phosphoryl-, phosphorothioyl- or phosphonioguanidines **6**−**7** (Scheme 3).[15,16] The conditions applied depend on the acidity of the ammonium salts used, their reactivities decreasing in the order [PhNH$_3$]Cl (pK_a = 4.63), morpholinium hydrochloride (morph·HCl) (pK_a = 8.21), benzylammonium chloride (pK_a = 9.33) and [*t*BuNH$_3$]Cl (pK_a = 10.83). The aryl and morpholinium compounds **4** rearranged even in acetonitrile at reflux, but in the case of the alkylammonium salts the rearrangement took place only at temperatures higher than the melting point of **4**.



Compound	Y	R	R'	Yield (%)
6a	O	–(CH$_2$)$_2$–O–(CH$_2$)$_2$–		55
6b	O	*t*Bu	H	38
6c	O	Ph	H	61
6d	S	–(CH$_2$)$_2$–O–(CH$_2$)$_2$–		55
6e	S	*t*Bu	H	82
6f	S	Ph	H	80
7a	–	–(CH$_2$)$_2$–O–(CH$_2$)$_2$–		76
7b	–	Ph	H	81

Scheme 3. Synthesis and selected examples of phosphoryl-, phosphorothioyl- and phosphonioguanidines **6**−**7**[15,16]

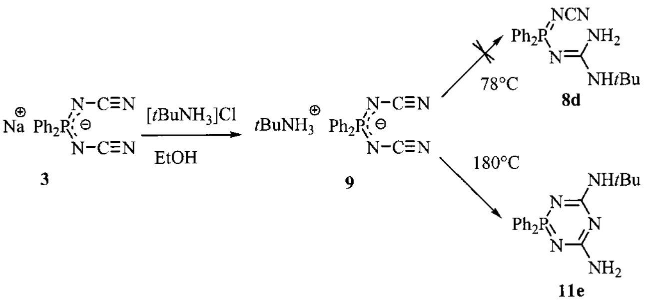
Similar behaviour may be expected for **3**, but the reaction with primary or secondary ammonium salts may be carried out either with only one or with both NCN groups, yielding phosphorus-functionalised mono- or diguanidines. At first we studied the behaviour of **3** in ethanol towards 1 equiv. of an ammonium salt [RNH$_3$]Cl (R = Ph, PhCH$_2$) and morpholine hydrochloride, respectively (Scheme 4). In order to favour the 1:1 reaction we used a 30% excess of **3** and monitored the reaction by ^{31}P NMR spectroscopy. Reaction conditions (temperature, time) varied according to the pK_a values of the ammonium salts used. At 20 °C with aniline hydrochloride the reaction was complete after 24 h, whereas in the case of benzylamine hydrochloride the reaction was achieved after 72 h of heating at 78 °C. The resulting guanidines **8** were isolated in yields ranging from 36 to 66% after recrystallisation.



Compound	R	R'	Yield (%)
8a	$-(CH_2)_2-O-(CH_2)_2-$		63
8b	$PhCH_2$	H	36
8c	Ph	H	66

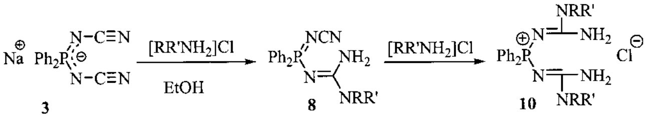
Scheme 4. Synthesis of (*N*-cyano-*P*,*P*-diphenylphosphorimidoyl)guanidines **8**

Nevertheless, primary ammonium chlorides such as *tert*-butylamine hydrochloride, being slightly less acidic than benzylamine hydrochloride, showed different behaviour. After combination of **3** and [tBuNH$_3$]Cl, the only product isolated was compound **9** {[tBuNH$_3$][Ph$_2$P(NCN)$_2$]}, in a yield of 71%. The ammonium salt **9** is stable in boiling ethanol, and formation of the corresponding guanidine **8d** could not be established even after a few days (Scheme 5).



Scheme 5. Synthesis of ammonium salt **9** and 1,3,5,2λ^5-triazaphosphinine **11e**

In the presence of a sixfold excess of the ammonium salts [RNH$_3$]Cl at either 20 °C (R = Ph) or 78 °C (R = PhCH$_2$ or morpholine hydrochloride, Scheme 6), on the other hand, addition reactions on both NCN groups took place, and diguanidinodiphenylphosphonium chlorides **10a−10c** could be isolated after recrystallisation in yields between 42 and 55% (Scheme 6). The reaction course was studied by ^{31}P NMR spectroscopy. At first the resonance signal of the monoguanidine **8** was observed, disappearing again after formation of **10**. As already discussed above, [PhNH$_3$]Cl reacts more rapidly (20 h, 25 °C) than [PhCH$_2$NH$_3$]Cl (10 d, 78 °C) because of the different basic strengths of the related amines.



R	R'	Compound	^{31}P NMR δ (ppm)	Compound	^{31}P NMR δ (ppm)	Yield %
$-(CH_2)_2-O-(CH_2)_2-$		**8a**	16.7	**10a**	9.3	45
$PhCH_2$	H	**8b**	17.2	**10b**	9.4	42
Ph	H	**8c**	16.8	**10c**	10.1	55

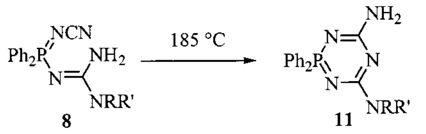
Scheme 6. Synthesis of diguanidinodiphenylphosphonium chlorides **10**

Synthesis of 1,3,5,2λ^5-Triazaphosphinines

Different routes to 1,3,5,2λ^5-triazaphosphinines have been described in the literature,[17−20] but no intramolecular cyclisation had been reported until now. Most of these compounds were isolated from reactions between phosphorus halides PCl$_{5-n}$Ph$_n$ ($n = 0-2$) and dicyanamide or amidines, resulting in 1,3,5,2λ^5-triazaphosphinines bearing halogen substituents at the ring carbon and phosphorus atoms. These halotriazaphosphinines react with various nucleophiles such as amines,[21,22] phenols,[23] alcohols[24] or sulfides[25] and yield the corresponding substituted heterocycles. It is worth noting that only a few 4,6-diamino-1,3,5,2λ^5-triazaphosphinines have so far been synthesised.

For Ph$_2$P(Y)N=C(NH$_2$)NHPh (Y = O, S) in the crystalline state, intramolecular hydrogen bonds of the N−H···Y type between the NH$_2$ group and the chalcogen atom have been observed, resulting in the formation of a almost planar six-membered ring.[26] A comparable geometry was also to be expected for the *N*-cyanophosphorimidoyl homologues Ph$_2$P(NCN)N=C(NH$_2$)NHR **8a−8c**; thus, an intramolecular nucleophilic attack of the −NH$_2$ nitrogen atom on the carbon atom of the NCN group should be possible.

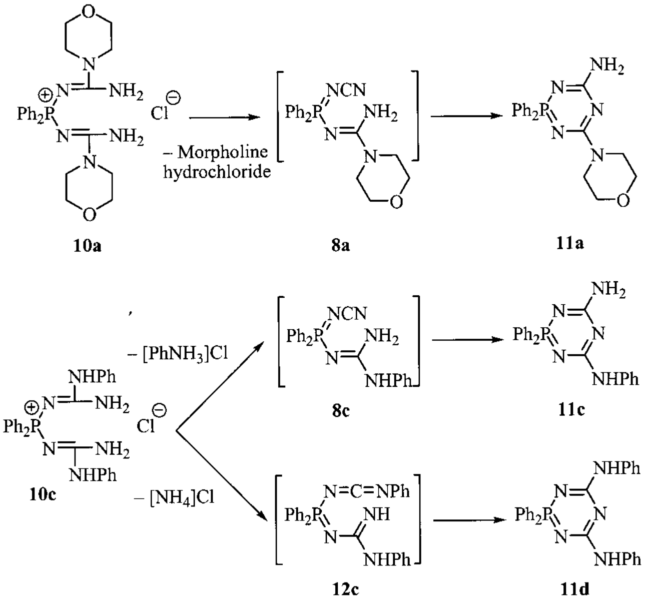
According to the same procedure as used for the conversion of alkylammonium cyanophosphorylazanide [RNH$_3$][Ph$_2$P(O)NCN] into the corresponding (diphenylphosphoryl)guanidines **6**,[13] we heated the ammonium salt **9** (Scheme 5) up to 185 °C in the absence of solvent for 25 min, and a rearrangement to 1,3,5,2λ^5-triazaphosphinine **11e** occurred. After purification by column chromatography, we isolated **11e** in a yield of 44%. The guanidine **8d** could not be clearly detected in the crude product but it can reasonably be postulated as an intermediate in the ring-closure reaction (Scheme 5). In support of this hypothesis, heating of the guanidines **8a−8c** up to 185 °C resulted in the formation of 1,3,5,2λ^5-triazaphosphinines **11a−11c**, which could be isolated in good yields, varying from 75 to 90%, after purification by column chromatography (Scheme 7).



Compound	R	R'	^{31}P NMR δ (ppm)	Yield (%)
11a	$-(CH_2)_2-O-(CH_2)_2-$		33.0	90
11b	$PhCH_2$	H	33.2	78
11c	Ph	H	32.4	75

Scheme 7. Synthesis of the 1,3,5,2λ^5-triazaphosphinines **11a−11c** starting from **8a−8c**

The behaviour of the diguanidinodiphenylphosphonium chlorides **10a** and **10c** at 185 °C is depicted in Scheme 8. According to a differential thermal analysis, compound **10c** decomposed at its melting point (218−223 °C) with a mass loss of 15.8%, corresponding to the evolution of aniline hydrochloride and ammonium chloride, and produced **11c** and **11d** in yields of 50 and 20%. The formation of two different heterocycles (**11c**, **11d**) can be understood by the fact that the liberation of both ammonium chloride and aniline hydrochloride gave the intermediates **8c** and **12c**, thus cyclising to afford both the non-symmetrical *N*-monophenyl and the symmetrical *N,N'*-diphenyl derivatives.



Compound	^{31}P NMR δ (ppm)	Yield (%)
11a	33.0	41
11c	32.4	50
11d	31.9	20

Scheme 8. Synthesis of the 1,3,5,$2\lambda^5$-triazaphosphinines **11a−c** starting from diguanidinophosphonium chlorides **10a−c** and postulated intermediates

In the case of the morpholine-modified diguanidinodiphenylphosphonium chloride **10a**, on the other hand, only one outcome of the reaction is possible, because the formation of a carbodiimide corresponding with **12c** is ruled out. Therefore, exclusively one product (**11a**) can be expected from this ring-closure reaction (Scheme 8).

Crystal and Molecular Structure of 11a

The molecular structure, the labelling scheme and selected geometric parameters of 6-amino-4-morpholino-2,2-diphenyl-1,3,5,$2\lambda^5$-triazaphosphinine (**11a**) are shown in Figure 1 and Table 2; the crystallographic data and refinement details are summarised in the Exp. Sect. Crystal structures of differently substituted 1,3,5,$2\lambda^5$-triazaphosphinines have already been described in the literature.[27−33]

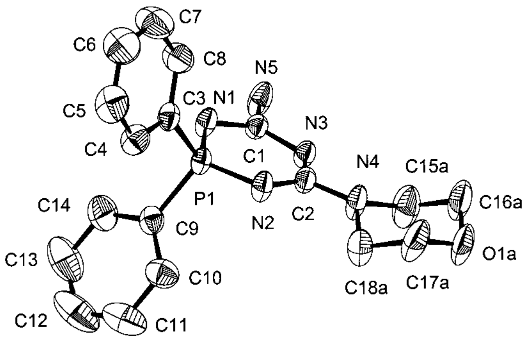


Figure 1. Molecular structure of the 1,3,5,$2\lambda^5$-triazaphosphinine **11a** (H atoms are omitted for clarity)

Table 2. Selected bond lengths [Å] and angles [°] for compound **11a**

P(1)−N(1)	1.607(2)	N(4)−C(2)	1.346(3)
P(1)−N(2)	1.610(2)	N(5)−C(1)	1.329(3)
P(1)−C(3)	1.797(2)		
P(1)−C(9)	1.800(3)		
N(1)−C(1)	1.343(3)	N(4)−C(18a)	1.480(4)
N(2)−C(2)	1.339(3)	N(4)−C(15a)	1.481(5)
N(3)−C(2)	1.338(3)	N(4)−C(18b)	1.475(5)
N(3)−C(1)	1.345(3)	N(4)−C(15b)	1.485(4)
N(1)−P(1)−N(2)	112.90(10)	N(1)−C(1)−N(3)	128.3(2)
N(1)−P(1)−C(3)	107.45(11)	N(3)−C(2)−N(2)	128.9(2)
N(2)−P(1)−C(3)	111.04(11)	N(3)−C(2)−N(4)	115.1(2)
N(2)−P(1)−C(9)	108.98(12)	N(2)−C(2)−N(4)	116.0(2)
N(1)−P(1)−C(9)	110.84(11)	C(2)−N(4)−C(18a)	121.3(3)
C(3)−P(1)−C(9)	105.38(11)	C(2)−N(4)−C(15a)	123.0(3)
C(1)−N(1)−P(1)	114.9(2)	C(18A)−N(4)−C(15a)	110.0(4)
C(2)−N(2)−P(1)	114.9(2)	C(2)−N(4)−C(18b)	123.4(3)
C(2)−N(3)−C(1)	118.7(2)	C(2)−N(4)−C(15b)	121.3(3)
N(5)−C(1)−N(1)	116.2(2)	C(18B)−N(4)−C(15b)	109.9(3)
N(5)−C(1)−N(3)	115.5(2)		

The phosphorus atom shown adopts a distorted tetrahedral geometry, with maximum and minimum angles between N(1)−P(1)−N(1) [= 112.90(10)°] and C(3)−P(1)−C(9) [= 105.38(11)°], respectively. The P(1)−C(3) [= 1.797(2) Å] and P(1)−C(9) [= 1.800(3) Å] bond lengths correspond with observed values for P(4)−C(arom.).[34,35] The P(1)−N(1) [= 1.607(2) Å] and P(1)−N(2) [= 1.610(2) Å] distances are somewhat longer than those expected for the P=N bond type (= 1.55 Å),[34] but they are in good agreement with these distances measured in other triazaphosphinines such as 2,2-dichloro-4,6-bis(trifluoromethyl)- [1.616(2) Å][26] or 2,2-bis(diisopropylamino)-4,6-diphenyl-1,3,5,$2\lambda^5$-triazaphosphinine [1.630(2) Å].[32] The mean value for the endocyclic C=N bond lengths was 1.341(3) Å, which corresponded to those in pyrimidines[32] and triazaphosphinines.[26−32] The P-heterocycle is almost planar; the maximum deviations from the mean plane (formed by the six ring atoms) amounting to 0.0829(5) Å and −0.068(2) Å for P(1) and N(1), respectively. Moreover, the exocyclic atoms N(4) and N(5) deviate only slightly from this plane [−0.094(2) and 0.003(3) Å] and, at the same time, the C(1)−N(5) [= 1.329(3) Å] and C(2)−N(4) [= 1.346(3) Å] bonds are shorter than expected: C(sp^2)−N(sp^3) = 1.43 Å.[34] The ring atoms of the morpholine ring from C(15a/b) to C(18a/b) and O(1a/b) are disordered; both positions are split with occupation factors of 50%. Both rings have a chair conformation, which, however, are oppositely folded with dihedral angles N(4)−C(15a/b)−C(16a/b)−O(1a/b) = 60.2(7)°/−59.6(7)°.

Within the lattice the phosphinine molecules are held together by intermolecular hydrogen bonds N(5)−H(1)···O(1a/b)′ ($1 - x$, $0.5 + y$, $1.5 - z$) with proton donor−acceptor distances N1···O(1a/b)′ = 3.034(8)/2.908(9) Å and angles N(5)−H(1)···O(1)′ = 166(2)/174(3)°.

Conclusion

The sodium phosphonium diylide **3** is of special interest as a precursor for new types of phosphorylated guanidines **8** and **10**. This study complements the application of phosphorylated cyanamides as synthetic tools towards *P*-functionalised guanidines.[15] Finally, the use of (*N*-cyanophosphorimidoyl)guanidines **8** and diguanidinophosphonium chlorides **10** as a precursor for 1,3,5,2λ^5-triazaphosphinines **11** represents an interesting alternative route to these heterocycles. All these molecules, especially the 1,3,5,2λ^5-triazaphosphinines **11**, because they are 1,3,5-triazine analogues, could find agricultural applications.[36]

Experimental Section

General Remarks: The starting materials were purchased from commercial sources and were used without further purification, unless mentioned otherwise. Acetonitrile was distilled from phosphorus pentoxide, and tetrahydrofuran from sodium/benzophenone. Melting points are uncorrected. Fast atom bombardment (FAB) MS was carried out with a JEOL JMS-DX 300 apparatus in a *m*-nitrobenzyl alcohol matrix. ^{1}H NMR spectra were recorded at 200 MHz. ^{13}C NMR spectra were recorded at 50.3 MHz with use of the JMOD pulse sequence. ^{31}P NMR spectra were recorded at 80 MHz.

Sodium Cyano (*N*-cyano-*P,P*-diphenylphosphorimidoyl)azanide (3): A solution of cyanic azide (65 mmol) in dry acetonitrile (80 mL), prepared by a known method,[14] was added at −30 °C to a stirred solution of sodium diphenyl phosphide[37] (65 mmol) in THF (80 mL) under nitrogen. After collection of about 90% of the theoretical volume of N_2 in a gas burette, the mixture was stirred at 25 °C for 12 h to complete the reaction and to avoid residual N_3CN. Subsequently, the yellow solution was filtered through Celite and the solvent was removed under reduced pressure. The residual brown oil was taken up in 1,4-dioxane (30 mL). After about 12 h at room temperature, the white solid obtained was filtered off and dried under vacuum. It was analytically pure. Yield 14.99 g (52 mmol, 80%). White solid, m.p. 182−184 °C (dioxane). IR (KBr): $\tilde{\nu}$ = 2190, 2140 (NCN) cm^{-1}. ^{31}P NMR ([D$_6$]DMSO): δ = 19.23 ppm. ^{15}N NMR ([D$_6$]DMSO): δ = −219.27 (d, $^3J_{N,P}$ = 2.32 Hz, CN), −339.45 (d, $^1J_{N,P}$ = 29.5 Hz, CN) ppm. ^{1}H NMR ([D$_6$]DMSO): δ = 7.4 (m, 4 H, aromatic H), 7.8 (m, 6 H, aromatic H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 119.3 (*C*N), 128.4 (d, $^3J_{P,C}$ = 12.6 Hz, *m*-C), 131.0 (d, $^2J_{P,C}$ = 9.6 Hz, *o*-C), 131.5 (d, $^4J_{P,C}$ = 2.3 Hz, *p*-C), 133.1 (d, $^1J_{P,C}$ = 129.3 Hz, *ipso*-C) ppm. FAB$^+$ MS: *m*/*z* (%) = 289 (15). FAB$^-$ MS: *m*/*z* (%) = 265 (100). $C_{14}H_{10}N_4NaP$ (288): calcd. C 58.37, H 3.50, N 19.45; found C 58.35, H 3.81, N 19.13.

General Procedure for the Synthesis of the (*N*-Cyano-*P,P*-diphenylphosphorimidoyl)guanidines 8a−c: A mixture of **3** (5 mmol) and the corresponding amine hydrochloride (3.5 mmol) in dry ethanol (20 mL) was placed in the reaction vessel. Reaction times and temperatures depended on the amine hydrochloride (see below). The reaction was monitored by ^{31}P NMR spectroscopy. After completion of the reaction, the solvent was evaporated under vacuum, and the oily residue was partitioned between water and chloroform. The organic layer was separated and dried with Na_2SO_4. Filtration and concentration, followed by recrystallisation of the crude product in a minimal volume of acetonitrile, afforded the guanidines **8**.

***N′*-(*N*-Cyano-*P,P*-diphenylphosphorimidoyl)morpholine-4-carboximidamide (8a):** Reaction time: 6 h at 78 °C. Yield: 0.77 g, 2.2 mmol, 63%. White solid, m.p. 193−195 °C (acetonitrile). IR (KBr): $\tilde{\nu}$ = 3420 (NH$_2$), 3280 (NH$_2$), 3180 (NH), 1635 (C=N), 2160 (CN) cm^{-1}. ^{31}P NMR (CDCl$_3$): δ = 16.70 ppm. ^{1}H NMR (CDCl$_3$): δ = 3.61 (m, 4 H, C*H*$_2$N), 3.68 (m, 4 H, C*H*$_2$O), 6.5 (s, 2 H, N*H*$_2$), 7.5 (m, 6 H, aromatic H), 7.8 (m, 4 H, aromatic H) ppm. ^{13}C NMR (CDCl$_3$): δ = 44.9 (*C*H$_2$N), 66.3 (*C*H$_2$O), 120.6 (*C*N), 128.7 (d, $^3J_{P,C}$ = 13.2 Hz, *m*-C), 131.2 (d, $^2J_{P,C}$ = 10.1 Hz, *o*-C), 131.3 (d, $^1J_{P,C}$ = 132.3 Hz, *ipso*-C), 132.0 (d, $^4J_{P,C}$ = 2.5 Hz, *p*-C), 157.2 (C=N) ppm. FAB$^+$ MS: *m*/*z* (%) = 354 (100). $C_{18}H_{20}N_5OP$ (353): calcd. C 61.18, H 5.70, N 19.81; found C 60.98, H 5.75, N 19.72.

***N*-[Amino(benzylamino)methylene]-*N′*-cyano-*P,P*-dimethylphosphinimidic Amide (8b):** Reaction time: 72 h at 78 °C. Yield: 0.46 g, 1.2 mmol, 36%. White solid, m.p. 155−156 °C (acetonitrile). IR (KBr): $\tilde{\nu}$ = 3450 (NH$_2$), 3305 (NH$_2$), 3180 (NH), 2150 (CN), 1615 (C=N) cm^{-1}. ^{31}P NMR (CDCl$_3$): δ = 17.2 ppm. ^{1}H NMR (CDCl$_3$): δ = 4.45 (d, J = 5.6 Hz, 2 H, PhC*H*$_2$), 6.05 (s, 2 H, N*H*$_2$), 7.03 (br. s, 1 H, N*H*), 7.35 (m, 5 H, aromatic H), 7.4 (m, 6 H, aromatic H), 7.8 (m, 4 H, aromatic H) ppm. ^{13}C NMR (CDCl$_3$): δ = 45.1 (Ph*C*H$_2$), 121.3 (*C*N), 127.0 (*p*-C), 127.2 (*o*-C), 128.4 (*ipso*-C), 128.5 (*m*-C), 128.5 (d, $^3J_{P,C}$ = 13.2 Hz, *m*-C), 131.3 (d, $^2J_{P,C}$ = 10.1 Hz, *o*-C), 131.8 (d, $^4J_{P,C}$ = 2.8 Hz, *p*-C), 131.9 (d, $^1J_{P,C}$ = 131.6 Hz, *ipso*-C), 158.7 (*C*=N) ppm. FAB$^+$ MS: *m*/*z* (%) = 374 (100). $C_{21}H_{20}N_5P$ (373): calcd. C 67.54, H 5.40, N 18.76; found C 67.62, H 5.40, N 18.27.

***N*-[(Amino(anilino)methylene]-*N′*-cyano-*P,P*-dimethylphosphinimidic Amide (8c):** Reaction time: 24 h at 20 °C. Yield: 0.82 g, 2.31 mmol, 66%. White solid, m.p. 193−195 °C (acetonitrile). IR (KBr): $\tilde{\nu}$ = 3410 (NH$_2$), 3300 (NH$_2$), 3200 (NH), 2140 (CN), 1630 (C=N) cm^{-1}. ^{31}P NMR (CDCl$_3$): δ = 16.8 ppm. ^{1}H NMR (CDCl$_3$): δ = 6.5 (s, 2 H, N*H*$_2$), 7.1 (t, J = 7.2 Hz, 1 H, aromatic H), 7.4 (m, 2 H, aromatic H), 7.6 (m, 8 H, aromatic H), 7.7 (m, 4 H, aromatic H), 9.3 (d, J = 5.6 Hz, 1 H, N*H*) ppm. ^{13}C NMR (CDCl$_3$): δ = 118.4 (*C*N), 121.3 (*m*-C), 123.7 (*p*-C), 128.7 (*o*-C), 128.8 (d, $^2J_{P,C}$ = 7.5 Hz), 130.9 (d, $^3J_{P,C}$ = 9.8 Hz), 131.8 (d, $^1J_{P,C}$ = 129.8 Hz, *ipso*-C), 132.0 (d, $^4J_{P,C}$ = 2.6 Hz), 138.4 (*ipso*-C), 158.9 (*C*=N) ppm. FAB$^+$ MS: *m*/*z* (%) = 360 (100). $C_{20}H_{18}N_5P$ (359): calcd. C 66.84, H 5.04, N 19.43; found C 66.42, H 5.44, N 18.22.

***tert*-Butylammonium Cyano(*N*-cyano-*P,P*-diphenylphosphorimidoyl)azanide (9):** A mixture of **3** (10 mmol) and *tert*-butylammonium chloride (10 mmol) in dry ethanol (50 mL) was stirred at 25 °C for 20 h. The sodium chloride was removed by filtration, and the filtrate was concentrated under vacuum, leaving a viscous colourless oil, which crystallised from acetonitrile. Yield: 2.4 g, 7.1 mmol, 71%. White solid, m.p. 169−170 °C (acetonitrile). IR (KBr): $\tilde{\nu}$ = 3400 (NH_2), 2180 (CN), 2160 (CN) cm^{-1}. ^{31}P NMR ($CDCl_3$): δ = 21.9 ppm. ^{1}H NMR ($CDCl_3$): δ = 1.2 [s, 9 H, (CH_3)$_3$C]), 7.4 (m, 6 H, aromatic H), 7.8 (m, 4 H, aromatic H) ppm. $C_{18}H_{22}N_5P$ (339): calcd. C 63.70, H 6.53, N 20.64; found C 62.79, H 6.34. N 20.29.

General Procedure for the Synthesis of the Diguanidinodiphenylphosphonium Chlorides 10a−c: A mixture of diylide **3** (2.5 mmol) and the corresponding amine hydrochloride (15 mmol) was stirred in dry ethanol (50 mL). Reaction times and temperatures depended on the amine hydrochloride (see below). The reaction was monitored by ^{31}P NMR, and after full disappearance of the diylide **3**, the reaction was quenched by concentration under vacuum, the oily residue then being taken up in H_2O and $CHCl_3$. The organic layer was separated, washed with water and dried (Na_2SO_4). Filtration and concentration, followed by recrystallisation of the crude product in a minimal volume of ethyl acetate, afforded the guanidines **10a−c**.

Bis{[amino(morpholino-4-yl)methylene]amino}diphenylphosphonium Chloride (10a): Reaction time 15 h at 78 °C. Yield: 0.54 g, 1.13 mmol, 45%. White solid, m.p. 199−201 °C (ethyl acetate). IR (KBr): $\tilde{\nu}$ = 3490 (NH_2), 3410 (NH_2), 3370 (NH_2), 3120 (NH), 1640 (C=N) cm^{-1}. ^{31}P NMR ($CDCl_3$): δ = 9.31 ppm. ^{1}H NMR ($CDCl_3$): δ = 3.7 (m, 8, CH_2N), 3.8 (m, 8 H, CH_2O), 6.6 (s, 4 H, NH_2), 7.45 (m, 6 H, aromatic H), 7.7 (m, 4 H, aromatic H) ppm. ^{13}C NMR ($CDCl_3$): δ = 43.5 (CH_2N), 66.3 (CH_2O), 128.9 (d, $^3J_{P,C}$ = 12.9 Hz, *m*-C), 131.1 (d, $^2J_{P,C}$ = 9.9 Hz, *o*-C), 131.3 (d, $^1J_{P,C}$ = 132.0 Hz, *ipso*-C), 131.9 (d, $^4J_{P,C}$ = 2.3 Hz, *p*-C), 157.2 (C=N) ppm. FAB$^+$ MS: *m*/*z* (%) = 441 (100) [$M^+ - Cl^-$]. $C_{22}H_{30}ClN_6O_2P$ (476.5): calcd. C 55.40, H 6.34, N 17.62; found C 54.98, H 6.37, N 17.35.

Bis{[amino(benzylamino)methylene]amino}diphenylphosphonium Chloride (10b): Reaction time: 10 d at 78 °C. Yield: 0.55 g, 1.1 mmol, 42%. White solid, m.p. 194−195 °C (ethyl acetate). IR (KBr): $\tilde{\nu}$ = 3475 (NH_2), 3440 (NH_2), 3260 (NH_2), 3130 (NH), 1630 (C=N) cm^{-1}. ^{31}P NMR ($CDCl_3$): δ = 9.44 ppm. ^{1}H NMR ($CDCl_3$): δ = 4.53 (d, *J* = 5.81 Hz, 4 H, CH_2Ph), 4.87 (s, 4 H, NH_2), 7.4 (m, 16 H, aromatic H), 8.3 (sl, 2 H, N*H*) ppm. ^{13}C NMR ([D$_6$]methanol): δ = 46.2 (CH_2), 128.2 (*o*-C), 128.3 (*p*-C), 129.7 (*m*-C), 129.8 (d, $^3J_{P,C}$ = 12.8 Hz, *m*-C), 132.6 (d, $^2J_{P,C}$ = 10.1 Hz, *o*-C), 132.8 (d, $^1J_{P,C}$ = 131.9 Hz, *ipso*-C), 133.2 (d, $^4J_{P,C}$ = 2.9 Hz, *p*-C), 140.8 (*ipso*-C), 160.1 (C=N) ppm. FAB$^+$ MS: *m*/*z* (%) = 481 (100) [$M^+ - Cl^-$]. $C_{28}H_{30}ClN_6P$ (516.5): calcd. C 66.05, H 5.85, N 16.26; found C 65.17, H 6.13, N 16.25.

Bis{[amino(anilino)methylene]amino}diphenylphosphonium Chloride (10c): Reaction time: 25 h at 20 °C. Yield: 0.67 g, 1.4 mmol, 55%. White solid, m.p. 222−223 °C (ethyl acetate). IR (KBr): $\tilde{\nu}$ = 3445 (NH_2), 3395 (NH_2), 3295 (NH_2), 3180 (NH), 1625 (C=N) cm^{-1}. ^{31}P NMR ($CDCl_3$): δ = 10.1 ppm. ^{1}H NMR ($CDCl_3$): δ = 6.2 (br. s, 4 H, NH_2), 7.1 (m, 2 H, aromatic H), 7.3 (m, 4 H, aromatic H), 7.4 (m, 6 H, aromatic H), 7.7 (m, 6 H, aromatic H), 9.8 (d, *J* = 1.6 Hz, 2 H, N*H*) ppm. ^{13}C NMR ($CDCl_3$): δ = 121.9 (*m*-C), 124.3 (*p*-C), 128.7 (*o*-C), 129.1 (d, $^3J_{P,C}$ = 13.2 Hz, *m*-C), 130.7 (d, $^1J_{P,C}$ = 132.2 Hz, *ipso*-C), 131.4 (d, $^2J_{P,C}$ = 10.4 Hz, *o*-C), 132.5 (d, $^4J_{P,C}$ = 2.9 Hz, *p*-C), 138.1 (*ipso*-C), 156.8 (C=N) ppm. FAB$^+$ MS: *m*/*z* (%) = 453 (100) [$M^+ - Cl^-$]. $C_{26}H_{26}ClN_6P$ (488.5): calcd. C 63.86, H 5.36, N 17.19; found C 63.54, H 5.28, N 16.97.

General Procedure for the Synthesis of the 2,2-Diphenyl-1,3,5,2λ^5-triazaphosphinines 11: Diguanidinophosphonium chloride **10** (Procedure a), (*N*-cyanophosphorimidoyl)guanidine **8** (Procedure b), or *tert*-butylammonium phosphonium diylide (2.5 mmol) **9** were heated at 180 °C under reduced pressure under nitrogen for 25 min. After cooling, the colourless glass was dissolved in chloroform (15 mL) and this solution was concentrated in vacuo. The products were purified as follows: Procedure a gave a mixture of two 1,3,5,2λ^5-triazaphosphinines, which were separated by chromatography on neutral alumina (eluent: ethyl acetate/methanol, 96:4). Procedure b gave the 4-alkylamino(arylamino)-6-amino-2,2-diphenyl-1,3,5,2λ^5-triazaphosphinines, which were purified by recrystallisation from the solvent given in parentheses.

6-(Morpholin-4-yl)-2,2-diphenyl-1,3,5,2λ^5-triazaphosphinine-4-amine (11a): Yield: 0.353 g, 1.0 mmol, 41% (Procedure a); 0.79 g, 2.25 mmol, 90% (procedure b). Colourless solid, m.p. 165−166 °C (ethyl acetate). IR (KBr): $\tilde{\nu}$ = 3380 (NH_2), 3295 (NH), 3185 (NH), 1630 (C=N) cm^{-1}. ^{31}P NMR ($CDCl_3$): δ = 33.06 ppm. ^{1}H NMR ($CDCl_3$): δ = 3.67 (m, 4 H, CH_2N), 3.81 (m, 4 H, CH_2O), 4.89 (d, *J* = 3.4 Hz, 2 H, NH_2), 7.5 (m, 6 H, aromatic H), 7.7 (m, 4 H, aromatic H) ppm. ^{13}C NMR ($CDCl_3$): δ = 43.7 (d, $^4J_{P,C}$ = 2.4 Hz, CH_2N), 66.9 (CH_2O), 128.4 (d, $^3J_{P,C}$ = 12.9 Hz, *m*-C), 130.8 (d, $^2J_{P,C}$ = 10.0 Hz, *o*-C), 131.6 (d, $^4J_{P,C}$ = 2.7 Hz, *p*-C), 134.0 (d, $^1J_{P,C}$ = 127.8 Hz, *ipso*-C), 164.8 (d, $^2J_{P,C}$ = 2.5 Hz, *C*=N), 167.1 (CNH_2) ppm. FAB$^+$ MS (NBA): *m*/*z* (%) = 354 (100). $C_{18}H_{20}N_5OP$ (353): calcd. C 61.8, H 5.70, N 19.81; found C 61.05, H 5.74, N 19.35.

X-ray Crystallographic Study of 6-(Morpholin-4-yl)-2,2-diphenyl-1,3,5,2λ^5-triazaphosphinine-4-amine (11a): Colourless, transparent prisms were grown from ethyl acetate. The X-ray measurement was performed with a STOE STADI4 diffractometer with use of graphite-monochromatised Mo-K_α radiation (λ = 0.71073 Å) at room temperature. The structure was solved by direct methods (SHELXS-86)[38] and refined with anisotropic displacement parameters for all non-H-atoms on F^2 (SHELXL-93).[39] All H-atoms were placed at their idealised positions; their parameters were refined isotropically according to the riding model. For the plot of the molecular structure the program DIAMOND[40] was used. $C_{18}H_{22}N_5OP$ (M_r = 353.36); crystal dimensions: 0.46 × 0.36 × 0.27 mm; monoclinic, *P*21/*c*; *a* = 8.889(1), *b* = 13.018(1), *c* = 16.925(2) Å, β = 104.03(1)°, *Z* = 4, *V* = 1900.1(3) Å^3, $\rho_{calcd.}$ = 1.235 g/cm^3, *T* = 293(2) K, *F*(000) = 744; intensities measured: 6664 (2.00° < θ < 24.95°); independent reflections: 3332 (R_{int} = 0.0203); observed reflections: 2555 [$I > 2\sigma(I)$]; $R_1/wR_2/S$ (observed data): 0.436/0.1076/1.115; $R_1/wR_2/S$ (all data): 0.0646/0.1268/1.111; maximum residual electron density was between −0.280 and 0.200 e·Å^{-3}. CCDC-221378 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

***N*-Benzyl-2,2-diphenyl-1,3,5,2λ^5-triazaphosphinine-4,6-diamine (11b):** Yield: 0.72 g, 1.95 mmol, 78% (Procedure b). Colourless solid, m.p. 178−179 °C (dichloromethane). IR (KBr): $\tilde{\nu}$ = 3480 (NH_2), 3265 (NH), 3100 (NH),1625 (C=N), 1570, 1330 (P=N) cm^{-1}. ^{31}P NMR ($CDCl_3$): δ = 33.28 ppm. ^{1}H NMR ($CDCl_3$): δ = 4.54 (s, 2 H, CH_2Ph), 5.54 (br. s, 2 H, NH_2), 6.28 (br. s, 1 H, N*H*), 7.25 (m, 5 H, aromatic H), 7.46 (m, 6 H, aromatic H), 7.62 (m, 4 H, aromatic H) ppm. ^{13}C NMR ($CDCl_3$): δ = 44.3 (d, $^4J_{P,C}$ = 2.7 Hz, CH_2Ph), 126.7 (*p*-C), 127.4 (*o*-C), 128.3 (d, $^3J_{P,C}$ = 12.9 Hz, *m*-C), 128.4 (*m*-C), 130.9 (d, $^2J_{P,C}$ = 10.1 Hz, *o*-C), 131.6 (d, $^4J_{P,C}$ = 2.7 Hz, *p*-C), 133.7 (d, $^1J_{P,C}$ = 127.8 Hz, *ipso*-C), 140.2 (*ipso*-C), 166.1 (CNH_2), 166.8 (C=N) ppm. FAB$^+$ MS: *m*/*z* (%) = 340 (100). $C_{21}H_{20}N_5P$ (339): calcd. C 67.55, H 5.40, N 18.76; found C 67.57, H 5.39, N 18.60.

***N*,2,2-Triphenyl-1,3,5,2λ^5-triazaphosphinine-4,6-diamine (11c):** Yield: (0.45 g, 1.25 mmol) 50%. (Procedure **a**), (0.67 g, 1.87 mmol) 75% (procedure **b**). White solid, m.p. 128−129 °C (ethyl acetate). IR (KBr): $\tilde{\nu}$ = 3460 (NH_2), 3400 (NH), 3380 (NH), 1630 (C=N). ^{31}P NMR ($CDCl_3$): δ = 32.37 ppm. ^1H NMR ($CDCl_3$): δ = 5.57 (d, J = 4.2 Hz, 2 H, NH_2), 6.95 (t, J = 7.3 Hz, 1 H aromatic H), 7.23 (t, J = 8.2 Hz, 2 H, aromatic H), 7.40 (m, 6 H, aromatic H), 7.62 (d, J = 7.76 Hz, 2 H, aromatic H), 7.8 (m, 5 H, aromatic H and N*H*) ppm. ^{13}C NMR ($CDCl_3$): 120.2 (*o*-C), 122.3 (*p*-C), 128.5 (d, $^3J_{C,P}$ = 13.0 Hz, *m*-C), 128.6 (*m*-C), 130.9 (d, $^2J_{C,P}$ = 10.3 Hz, *o*-C), 131.9 (d, $^4J_{C,P}$ = 2.7 Hz, *p*-C), 133.1 (d, $^1J_{C,P}$ = 120.3 Hz, *ipso*-C), 139.0 (*ipso*-C), 164.1 (*C*−NH_2), 166.9 (*C*=N) ppm. FAB$^+$ MS: *m*/*z* = 360 (100). $C_{20}H_{18}N_5P$ (359): calcd. C 66.84, H 5.05, N 19.49; found C 64.84, H 4.95, N 18.53.

***N*,*N*′,2,2-Tetraphenyl-1,3,5,2λ^5-triazaphosphinine-4,6-diamine (11d):** Yield: (0.44 g, 1 mmol) 20% (procedure **a**). Pale yellow solid, m.p. 201−202 °C (ethyl acetate). IR (KBr): $\tilde{\nu}$ = 3400 (NH), 1590 (C=N) cm^{-1}. ^{31}P NMR ($CDCl_3$): δ = 31.97 ppm. ^1H NMR ($CDCl_3$): δ = 7.03 (t, J = 7.3 Hz, 2 H, aromatic H), 7.28 (t, J = 7.5 Hz, 4 H, aromatic H), 7.51 (m, 6 H, aromatic H), 7.62 (d, J = 7.76 Hz, 4 H, aromatic H), 8.0 (m, 4 H, aromatic H), 8.1 (s, 2 H, N*H*) ppm. ^{13}C NMR ($CDCl_3$): 120.3 (*p*-C), 122.4 (*m*-C), 128.6 (d, $^3J_{C,P}$ = 13.0 Hz, *m*-C), 128.7 (*m*-C), 131.0 (d, $^2J_{C,P}$ = 10.2 Hz, *o*-C), 132.0 (d, $^4J_{C,P}$ = 2.7 Hz, *p*-C), 133.4 (d, $^1J_{C,P}$ = 128 Hz, *ipso*-C), 140.0 (*ipso*-C), 163.9 (*C*=N) ppm. FAB$^+$ MS: *m*/*z* = 436 (100). $C_{22}H_{26}N_5P$ (435): calcd. C 71.71, H 5.09, N 16.08; found C 71.14, H 5.24, N 15.87.

***N*-(*tert*-Butyl)-2,2-diphenyl-1,3,5,2λ^5-triazaphosphinine-4,6-diamine (11e):** Yield: 0.37 g, 1.1 mmol, 44%. White solid, m.p. 197−198 °C (methanol). IR (KBr): $\tilde{\nu}$ = 3390 (NH_2), 3300 (NH), 3160 (NH), 1640−1620 (C=N) cm^{-1}. ^{31}P NMR ($CDCl_3$): δ = 31.7 ppm. ^1H NMR ($CDCl_3$): δ = 1.42 [s, 9 H, $(CH_3)_3C$], 4.9 (br. s, 3 H, NH_2, N*H*), 7.40 (m, 6 H, aromatic H), 7.7 (m, 4 H, aromatic H) ppm. ^{13}C NMR ($CDCl_3$): δ = 29.5 [$(CH_3)_3C$], 50.6 [$(CH_3)_3C$], 128.4 (d, $^3J_{C,P}$ = 12.9 Hz, *m*-C), 130.6 (d, $^2J_{C,P}$ = 10.0 Hz, *o*-C), 131.6 (*p*-C), 134 (d, $^1J_{C,P}$ = 128.6 Hz, *ipso*-C), 165.1 (*C*NH_2), 166.3 (*C*=N) ppm. FAB$^+$ MS: *m*/*z* (%) = 340 [M$^+$] (100). $C_{18}H_{22}N_5P$ (339): calcd. C 63.70, H 6.53, N 20.63; found C 62.46, H 6.47, N 19.66.

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[1] O. I. Kolodiazhnyi, *Phosphorus Ylides*, Wiley-VCH, Weinheim, **1999**.
[2] H. Staudinger, J. Meyer, *Helv. Chim. Acta* **1919**, *2*, 635−646.
[3] H.-J. Cristau, *Chem. Rev.* **1994**, *94*, 1299−1313.
[4] H.-J. Cristau, C. Garcia, J. Kadoura, E. Toreilles, *Phosphorus, Sulfur Silicon Relat. Elem.* **1990**, *49*/*50*, 151−154.
[5] H.-J. Cristau, M. Taillefer, I. Jouanin, *Synthesis* **2001**, *1*, 69−74.
[6] M. Taillefer, N. Inguimbert, L. Jäger, K. Merzweiler, H.-J. Cristau, *Chem. Commun.* **1999**, 565−566.
[7] O. J. Scherer, P. Klusmann, *Angew. Chem.* **1968**, *14*, 560−561, *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 541−542.
[8] H.-J. Cristau, C. Garcia, *Synthesis* **1990**, *4*, 315−317.
[9] L. Jäger, H. Köhler, *Sulfur Rep.* **1992**, *12*, 159−212.
[10] L. Jäger, H. Köhler, A. I. Brusilovec, V. V. Skopenko, *Z. Anorg. Allg. Chem.* **1988**, *564*, 85−95.
[11] H. Köhler, D. Glanz, *Z. Anorg. Allg. Chem.* **1987**, *554*, 123−131.
[12] A. Steiner, S. Zacchini, P. Richards, *Coord. Chem. Rev.* **2002**, *227*, 193−216.
[13] H-J. Cristau, I. Jouanin, M. Taillefer, *J. Organomet. Chem.* **1999**, *584*, 68−72.
[14] F. D. Marsh, M. E. Hermes, *J. Am. Chem. Soc.* **1964**, *86*, 4506−4507.
[15] L. Jäger, N. Inguimbert, M. Taillefer, H-J. Cristau, *Synth. Commun.* **1995**, *25*, 2857−2864.
[16] N. Inguimbert, L. Jäger, M. Taillefer, H-J. Cristau, *J. Organomet. Chem.* **1997**, *529*, 257−265.
[17] A. Schmidpeter, J. Ebeling, *Angew. Chem.* **1967**, *79*, 534−535, *Angew. Chem. Int. Ed. Engl.* **1967**, 565.
[18] M. Becke-Goering, D. Jung, *Z. Anorg. Allg. Chem.* **1970**, *372*, 233−247.
[19] K. J. L. Paciorek, D. H. Harris, J. H. Nakahara, M. E. Smythe, R. H. Kratzer, *J. Fluorine Chem.* **1985**, *29*, 399−416.
[20] G. Alcaraz, V. Piquet, A. Baceireido, F. Dahan, W. W. Schoeller, G. Bertrand, *J. Am. Chem. Soc.* **1996**, *118*, 1060−1065.
[21] W. Pinkert, G. Schoening, O. Glemser, *Z. Anorg. Allg. Chem.* **1977**, *436*, 136−139.
[22] P. P. Kornuta, N. V. Kolotilo, L. N. Markovskii, *J. Gen. Chem. USSR* **1982**, *52*, 2418−2421.
[23] V. P. Kukar, T. N. Kasheva, *J. Gen. Chem. USSR* **1976**, *46*, 239−244.
[24] P. P. Kornuta, N. V. Kolotilo, L. N. Markovskii, *J. Gen. Chem. USSR* **1982**, *52*, 519−525.
[25] M. Meyer, U. Klingebiel, *Chem. Ber.* **1988**, *121*, 1119−1122.
[26] N. Inguimbert, M. Biedermann, H. Stoeckli-Evans, H. Hartung, A. Kolbe, M. Taillefer, L. Jäger, H. J. Cristau, *J. Mol. Struct.* **2000**, *519*, 211−218.
[27] I. E. Boldeskul, A. S. Tarasevich, A. E. Obodovskaya, Z. A. Starikova, P. P. Kornuta, *J. Gen. Chem. USSR (Engl. Transl.)* **1990**, *60*, 1763−1767.
[28] A. N. Chernega, I. E. Boldeskul, M. Yu. Antipin, Yu. T. J. Struchkov, *Struct. Chem. (Engl. Transl.)* **1990**, *31*, 363−365.
[29] S. J. Chen, K. Brychcy, U. Behrens, W. D. Stohrer, R. Mews, *Z. Naturforsch., Teil B* **1995**, *50*, 86−90.
[30] A. N. Chernega, I. E. Boldeskul, M. Yu. Antipin, Yu. T. Struchkov, P. P. Kornuta, M. V. Kolotilo, *J. Gen. Chem. USSR (Engl. Transl.)* **1987**, *57*, 1772−1777.
[31] F. Belaj, *Z. Naturforsch., Teil B* **1996**, *51*, 1428−1432.
[32] N. D. Reddy, A. J. Elias, A. Vij, *J. Chem. Soc., Dalton Trans.* **1999**, 1515−1518.
[33] G. Alcaraz, A. Baceireido, M. Nieger, W. W. Schoeller, G. Bertrand, *Inorg. Chem.* **1996**, *35*, 2458−2462.
[34] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc., Perkin Trans. 2* **1987**, S1−S19.
[35] P. Rademacher, *Strukturen Organischer Moleküle*, VCH, Weinheim, **1987**.
[36] A. F. Barlow, in P. T. Haskel (Ed.), *Pesticide Application Principles and Practice*, Oxford University Press, Oxford, **1985**, p. 1.
[37] E. C. Ashby, R. Gurumurthy, R. Ridlehuber, *J. Org. Chem.* **1993**, *58*, 5832−5837.
[38] SHELXS-86: G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.
[39] G. M. Sheldrick, *SHELXL-93, Program for the Refinement of Crystal Structures*, University of Göttingen, **1993**.
[40] K. Brandenburg, *DIAMOND*, Crystal Impact GbR, Visual Information System for Crystal Structures.

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