Mono-Phosphazenyl Phosphines (R₂N)₃P=N–P(NR₂)₂ –
Strong P-Bases, P-Donors, and P-Nucleophiles for the Construction
of Chelates

Julius F. Kögel,[a] Sebastian Ullrich,[a] Borislav Kovačević,[b] Sebastian Wagner,[a] and Jörg Sundermeyer*,[a]

Dedicated to Professor Manfred Scheer on the Occasion of his 65th Birthday

Abstract. We present a convenient three-step synthesis of amino substituted phosphazenyl phosphines of the general formula (R₂N)₃P=N–P(NR₂)₂ [NR₂ = N(CH₂)₄, N(CH₂)₅, N(CH₂)₆]. These easily accessible mixed valent compounds display a surprisingly high proton affinity and basicity in the same range as the corresponding Schwesinger diphosphazene (Me₂N)₃P=N–P=NEt(NMe₂)₂ (Et-P₂) and Verkade’s proazaphosphatrane superbases. Within the central [P(III)–N=P(IV)] scaffold, the phosphine P III and not the phosphazene N III atom is the center of highest proton affinity, basicity and donor strength. As P-bases, the title compounds display calculated proton affinities between 265.8 (NR₂ = NMe₂) and 274.7 kcal·mol⁻¹ [NR₂ = N(CH₂)₄] and p\textsubscript{KBH⁺} values between 26.4 (NR₂ = NMe₂) and 31.5 [NR₂ = N(CH₂)₄] on the acetonitrile scale. As P-nucleophiles, they are key intermediates in the synthesis of hyperbasic bis(diphosphazene) proton sponges, chiral bis(diphosphazene) proton pincers, bisphosphazides, and superbasic P₂-bisylides. Their Staudinger reactions as nucleophile towards 1,8-diazidonaphthalene leading to 1,8-naphthalene-bisphosphazides is described in detail. The donor strength of the title compounds towards fragments [Se] and [Ni(CO)₃] is in the same range as that of N-heterocyclic carbenes.

Introduction

Diphosphazenes have become commercially available and valuable synthetic tools in organic chemistry. As strong non-ionic proton acceptors these Schwesinger P₂-bases[1] can be superior to classical metal organic bases. They allow reactions to proceed with less side products and higher chemo- and stereoselectivity. This can be referred to their ability to generate weakly coordinated carbanions[2] such as applied in aldol reactions,[3] in the generation of S-ylides[4] or in sigmatropic rearrangements.[5]

The classical synthesis of Schwesinger P₂-bases does not involve P(III) intermediates and their Staudinger reaction with azides, mainly because this strategy would involve hazardous alkyl azides.[11] For this reason, phosphazeny1 phosphines, that could act as nitrene acceptors did not prominently move into the focus of scientific interest as starting materials in the two principle routes to Schwesinger bases (Scheme 1).[6] However, a report on the preparation of P₁-phosphazene bases via conversion of P(III) precursors with organic azides was published by Alexandrova et al.[7] We demonstrated that the Staudinger reaction between [(CH₂)₄N]₃P=N–P[N(CH₂)₄]₂ and 1,8-diazidonaphthalene yields the bisphosphazene proton sponge P₂-TPPN (Figure 1), the so far most basic representative of the class of chelating superbases.[1] As surprisingly stable intermediates of P₂-TPPN synthesis, the chelating P₂-bisphosphazide P₂-TPPN(2N₂) and corresponding dimethylamino substituted P₂-HMPPN(2N₂) with their two different binding sites for metal cations or H-bonded substrates were characterized.[9] Finally, mono-phosphazeny1 phosphines described in this paper are key intermediates in the synthesis of higher homologues of superbasic P₂-bisylides such as the so far unknown P₂-MHPN (Figure 1).[10]

Scheme 1. Synthetic value of the presented P₂-synthons for the preparation of Schwesinger P₂-bases.

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The second common synthetic strategy towards $P_2$-phosphazene bases is the Kirsanov reaction\(^{[11]}\) which describes the conversion of a primary amine with a $PV$-electrophile of the general formula [(R$_2$N)$_3$P=N–P(NR$_2$)$_2$X]+X$^-$ (X = Hal) in the presence of an auxiliary base (Scheme 1). Only recently, we could show the synthetic value of such phosphazencyl phosphate derived $P_2$-electrophiles [(Me$_2$N)$_3$P=N–P(NMe$_2$)$_2$Br]$^+$$\text{Br}^-$ and [((CH$_2$)$_4$N)$_3$P=N–P(N(CH$_2$)$_4$)$_2$Br]$^+$$\text{Br}^-$ for the preparation of chelating $C_2$-symmetric chiral superbases with a binaphthyl\(^{[12]}\) and a cyclohexyl spacer.\(^{[13]}\)

Species with the general formula (R$_2$N)$_3$P=N–P(NR$_2$)$_2$ exhibit remarkable basicity properties with proton affinities between 265.8 kcal mol$^{-1}$ for (NR$_2$ = NMe$_2$) and 274.7 kcal mol$^{-1}$ for [NR$_2$ = N(CH$_2$)$_4$] – see discussion below. In contrast to most superbases like amidines, guanidines, phosphazenes or proton sponges, the basicity center of the bases presented herein is the P$^{III}$ atom and not the adjacent phosphazene N$^{III}$ atom. This was not only found computationally, but also verified by X-ray crystallographic and NMR spectroscopic methods. Studies concerning the basicity of phosphazenes have been reported by Frenking\(^{[14]}\), Kolomeitsev\(^{[15]}\) and Koppel.\(^{[16]}\) One of the best-studied class of P-bases are Verkade’s proazaphosphatranes N(CH$_2$CH$_2$NR)$_3$P (e.g. PA = 261.0 kcal mol$^{-1}$ for R = CH$_3$).\(^{[17]}\) Phosphazene RN=P$^V$ derivatives of such phosphatranes have been successfully used as organocatalysts in 1,4-additions of nucleophiles,\(^{[18]}\) Stille couplings\(^{[19]}\) or the activation of trimethylsilyl cyanide.\(^{[20]}\) A very strong P-base, first synthesized as hydrate by Kirsanov, but not recognized as superbase for a long time, is [(Me$_2$N)$_3$P=N–P(NMe$_2$)$_2$Br]$^+$$\text{Br}^-$ with a proton affinity of 295.5 kcal mol$^{-1}$\(^{[17,21]}\). Other P-bases such as guanidino-substituted [(Me$_2$N)$_3$C=N]$^+P$ (PA = 278.8 kcal mol$^{-1}$)\(^{[17]}\) exhibit extremely high proton affinity, but have only been isolated in their protonated forms. The corresponding base turned out to be unstable so that their basic properties could only be studied by theory. However, Dielmann et al. presented an aromatically stabilized derivative tris(1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidenamino)phosphine (IAP) with an impressive experimental p$K_B^+$ of 38.8 on the acetonitrile scale.\(^{[22,23]}\) Recently, we described higher order tris-phosphazenylluminophosphines (tris-PAP) displaying even higher P-basicities than those of IAP or of corresponding Schwesinger N-bases with the same number of P-atoms. At the same time tris-PAP reveal higher Tolman electronic parameters (TEP) than any other neutral P-ligand (Figure 2).\(^{[24]}\)

As tris-PAP tend to be more basic and much stronger donors than needed for catalytic applications we are interested to develop the chemistry of more easily accessible mono-phosphazenyl phosphines (mono-PAP).

For R = alkyl and phenyl at phosphorus, mono-PAPs have been investigated previously.\(^{[25]}\) Much less is known about the all P-amino substituted derivatives put into focus here. With this publication, we provide deeper insight into the preparation of synthetically most valuable amino-substituted $P_2$-synthons, their NMR spectroscopic characteristics, their P-basicity and P-donor strength and to some extent also their structural features. A short note on [(Me$_2$N)$_3$P=N–P(NMe$_2$)$_2$Br]$^+$$\text{Br}^-$ and the pyrrolidino-substituted compounds [((CH$_2$)$_4$N)$_3$P=N–P(N(CH$_2$)$_4$)$_2$] and [((CH$_2$)$_3$N)$_3$P=N–P(N(CH$_2$)$_4$)$_2$Br]$^+$$\text{Br}^-$ has been included into the supporting information of our previous communications\(^{[8,9,12,13]}\) but full details of their reactive properties, spectroscopic and structural features as well as their intrinsic basicity and donor strength were not discussed.

Figure 1. $P_2$-building blocks in the synthesis of bisphosphazene proton sponge $P_2$-TPPN,\(^{[8]}\) the bisphosphazide $P_2$-HMPN(2N$_2$),\(^{[9]}\) chiral superbases\(^{[12,13]}\) and superbasic $P_2$-bisylides.\(^{[10]}\)

Figure 2. Examples of N-substituted p$K_B^+$ compounds with a very high basicity and donor strength.
Results and Discussion

Synthesis and Spectroscopy of $P_2$-Synthons

The mixed valent P-nucleophiles of general formula \((R_2N)_3P=N–P(NR_2)2\) (2–4) were prepared via three steps following the strategy laid out for parent \((Me_2N)_3P=N–P(NMe_2)2\) (1)\textsuperscript{[21]} starting from corresponding phosphorus(III) amides, their Staudinger reaction with TMS-N\(_3\), followed by condensation with PCl\(_3\) and aminolysis of \((R_2N)_3P=N–PCl_2\) with secondary amines. Oxidation of the $P_2$-nucleophiles \((R_2N)_3P=N–P(NR_2)2\) with bromine leads to an umpolung into $P_2$-electrophiles \([(R_2N)_3P=N–P(NR_2)2Br]+Br–\).

\((R_2N)_3P=N–SiMe3\) Derivatives

The Staudinger reaction with TMS-N\(_3\) is well documented for the preparation of alkyl- or aryl-substituted species such as Ph\(_3P=N–SiMe3\),\textsuperscript{[26]} Me\(_3P=N–SiMe3\)\textsuperscript{[27]} or \(t\)Bu\(_3P=N–SiMe3\)\textsuperscript{[28]} which have been used as precursors for strongly electron-donating phosphiniminato ligands, finally for proazaphosphatrane N(CH\(_2\)CH\(_2\)NCH\(_3\))\(_3P\)\textsuperscript{[29]}.

P-amino-substituted derivatives include \((Me_2N)_3P=N–SiMe3\),\textsuperscript{[21,30]} [(CH\(_2\))\(_4\)N]\(_3P=N–SiMe3\)\textsuperscript{[31]} and \((Et_2N)_3P=N–SiMe3\)\textsuperscript{[32]}.

The stability of initially formed phosphazides \((R_2N)_3P=N–N=N–SiMe3\) with respect to loss of molecular nitrogen depends on the bulkiness of substituents at the phosphorus atom. Whereas \((Me_2N)_3P=N–N=N–SiMe3\) eliminates \(N_2\) at room temperature, phosphazides bearing cyclic amino substituents require heating. Schlak et al. reported that a considerable amount of hardly separable \(P_2\)-byproduct \((Me_2N)_3P=N–P(NMe_2)2=N–SiMe3\) is formed in the course of the Staudinger reaction of \((MeN_2)3P\)\textsuperscript{[33]}.

We find, that analogous side products are only observed in trace amounts in our compounds with pyrrolidino, piperidino, or azepanyl groups (Scheme 2). The oxidation of the \(P^{\text{III}}\) atom leads to a strong high field shift in the \(^{31}P\) NMR spectrum. In both, \(P^{\text{III}}\) amides and \(P^{\text{V}}\) amid-imides, an increasing shielding of the phosphorus nucleus is observed in the order \(-NMe_2 < -N(CH_2)_6 < -N(CH_2)\)\(_4\) (Table 1).

\begin{table}
\caption{\(31^P\) and \(^{13}C\) NMR spectroscopic data \textsuperscript{a)} of iminophosphoranes \((R_2N)_3P=N–SiMe3\).
\begin{tabular}{cccccc}
Yield /\% & \(\delta^{\text{P}}\) & \(\delta^{\text{C}1}\) & \(\delta^{\text{C}2}\) & \(\delta^{\text{C}(\text{TMS})}\) & \(\text{J}^{\text{P,C}1}\) /Hz & \(\text{J}^{\text{P,C}2}\) /Hz & \(\text{J}^{\text{P,C}(\text{TMS})}\) /Hz \\
\hline
\((CH_2)\_3N\)_3P=N–SiMe3 & 79 & 0.7 & 46.8 & 4.3 & 26.7 & 7.9 & – & 5.0 & 2.7 \\
\((CH_2)\_3N\)_3P=N–SiMe3 & 84 & 8.4 & 43.6 & 1.6 & 26.9 & 6.5 & 25.5 & 4.8 & 2.5 \\
\((CH_2)\_3N\)_3P=N–SiMe3 & 77 & 10.6 & 48.9 & 3.7 & 31.1 & 5.4 & 27.3 & 4.8 & 2.0 \\
\end{tabular}
\textsuperscript{a)} All spectra were recorded in \([D_6]\)benzene.
\end{table}

\((R_2N)_3P=N–PCl2\) Derivatives

The second phosphorus atom was introduced via condensation of \((R_2N)_3P=N–SiMe3\) with PCl\(_3\) (Scheme 3). The products \((R_2N)_3P=N–P(NR_2)2\) are isolated in excellent yields as colorless solids. \(P^{\text{V}}\)-aryl and \(P^{\text{V}}\)-alkyl derivatives of this type were reported by Eckart et al. \textsuperscript{[34]} (Table 2).

\begin{table}
\caption{\(31^P\) NMR spectroscopic properties \textsuperscript{a)} of the mixed valent $P_2$-species \((R_2N)_3P=N–PCl2\).
\begin{tabular}{cccccc}
Yield /\% & \(\delta^{\text{P}^{\text{V}}}\) & \(\delta^{\text{P}^{\text{III}}}\) & \(\text{J}^{\text{P,P}}\) /Hz \\
\hline
\((CH_2)\_4N\)_3P=N–PCl2 & 92 & 10.5 & 143.0 & 84.6 \\
\((CH_2)\_5N\)_3P=N–PCl2 & 90 & 17.2 & 144.5 & 82.7 \\
\((CH_2)\_6N\)_3P=N–PCl2 & 100 & 20.6 & 145.2 & 88.2 \\
\((Me_2N)3P=N–PCl2\) & 89 & 23.1 & 145.0 & 81.3 \\
\end{tabular}
\textsuperscript{a)} All spectra were recorded in \([D_6]\)benzene.
\end{table}

\((R_2N)_3P=N–PCl_2\) Derivatives

In case of the piperidino- and azepanyl-substituted species, the substitution of the chlorine atoms of \((R_2N)_3P=N–PCl2\) was achieved by the reaction with four equivalents of the corresponding amine in diethyl ether (Scheme 4).
protonated superbasic proton sponge TMGN

exchange rates, since a 1:1 mixture of (Me2N)3P=N–P(NMe2)2
protonated by [H2NR2]Cl! Interestingly, this procedure did not
work for pyrrolidino derivative [(CH2)4N]3P=N–PCl2. The de-
separable side products and LiCl base adduct formation. The
sodium pyrrolidide. Using simple lithium pyrrolidide led to in-
volves most careful inert gas techniques and a final pentane
extraction step in order to get spectroscopically pure material.

The substitution of P–Cl for P-amino groups is accompanied
by a considerable high field shift of the corresponding 31P
NMR signal of formerly P III while the other 31P resonance
remains nearly unchanged. The 2Jpp coupling constants are
ranging from 81.3 to 121.3 Hz (Table 3). Both, the P III atoms’
chemical shifts and the 2Jpp coupling constants in mono-PAPs
are significantly lower than their respective tris-PAPs.[34]

In order to get a first impression on the basicity of phos-
phazeny1-phosphines 1–4 an NMR titration experiment using
protonated superbasic sponge TMGN·HPF6 was con-
ducted. 1,8-Bis(tetramethylguanidino)naphthalene (TMGN)
has experimental and calculated pKbH+ values in acetonitrile
of 25.1[35] and 25.4,[36] respectively. Quantitative deproton-
ation of TMGN by (Me2N)3P=N–P(NMe2)2 was con-
formed via 1H and 31P NMR spectroscopy. We did not observe
any proton self-exchange between base forms 1–4 and corre-
sponding acid forms [1–4]·HPF6. In contrast to Schwesinger’s
phosphazines, P III bases exhibit significant lower proton self-
exchange rates, since a 1:1 mixture of (Me2N)3P=N–P(NMe2)2
and its corresponding bis(triflyl)imide onium salt showed two
separated sets of signals in the 1H and 31P spectra in aceto-
nitrile at room temperature.

Two equivalents of the amine acted as a base with formation
of amine hydrochlorides. As the product is more basic than the
amine hydrochloride by-product, the lattice energy of precipit-
at ing hydrochloride from ether is an essential driving force:
In MeCN solution, the product (R2N)3P=N–P(NR2)2 is fully
protonated by [H2NR2]Cl! Interestingly, this procedure did not
work for pyrrolidino derivative [(CH2)4N]3P=N–PCl2. The de-
separable side products and LiCl base adduct formation. The
sodium pyrrolidide. Using simple lithium pyrrolidide led to in-
volves most careful inert gas techniques and a final pentane
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and its corresponding bis(triflyl)imide onium salt showed two
separated sets of signals in the 1H and 31P spectra in aceto-
nitrile at room temperature.

Table 3. 31P NMR spectroscopic properties a) of the mixed valent P 2-species (R2N)3P=N–P(NR2)2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield /%</th>
<th>δPIII /ppm</th>
<th>δP II /ppm</th>
<th>Jpp /Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(CH2)3N]3P=N–[N(CH2)4]2</td>
<td>86</td>
<td>10.2</td>
<td>93.7</td>
<td>102.1</td>
</tr>
<tr>
<td>[(CH2)3N]3P=N–[N(CH2)5]2</td>
<td>77</td>
<td>17.6</td>
<td>97.3</td>
<td>121.3</td>
</tr>
<tr>
<td>[(CH2)3N]3P=N–[N(CH2)6]2</td>
<td>59</td>
<td>20.0</td>
<td>100.3</td>
<td>118.8</td>
</tr>
<tr>
<td>(Me2N)3P=N–(NMe2)2</td>
<td>63</td>
<td>22.9</td>
<td>102.1</td>
<td>109.1</td>
</tr>
</tbody>
</table>

a) All spectra were recorded in [D6]benzene.

An umpolung of the highly nucleophilic phosphorus(III) atom is achieved by oxidation with bromine in benzene. For P1-synths this procedure had been reported by Issleib and Seidel (Scheme 5).[37] The ion or non-ionic nature of P1-species R3PBr2 has been disputed in the literature.[38] X-ray crys-
tallography, NMR spectroscopic studies, conductivity mea-
surements and the insolubility in nonpolar solvents revealed
that such compounds usually exhibit salt-like character with a
[R2PBr]+ cation and a bromide anion, and not covalent λ2-
phosphorane character. Since such trigonal bipyramidal struc-
ture is only found for species with strongly electron-with-
drawing substituents like in (F5C6)3PBr2,[38b] the bromophos-
phorane bromide character is plausible for the compounds
treated herein. This has been proven by XRD structure analy-
sis of [(Me2N)3P=N–P(NMe2)2]Br, vide infra. Furthermore,
only peaks for [(R2N)3P=N–P(NR2)2]Br+ cations, but no spe-
cies containing two bromine atoms were detected in ESI(+) mass spectra from acetonitrile. As expected, P-oxidation is ac-
companied by high-field shift of δP and a strong decrease of
the 2Jpp coupling constants (Table 4).

Table 4. 31P NMR spectroscopic properties a) of the P2-electrophiles [(R2N)3P=N–P(NR2)2]Br+.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield /%</th>
<th>δP II /ppm</th>
<th>Jpp /Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(R2N)3P=N–P(N(CH2)4)2]Br+</td>
<td>84</td>
<td>9.9</td>
<td>50.3</td>
</tr>
<tr>
<td>[(R2N)3P=N–P(N(CH2)5)2]Br+</td>
<td>88</td>
<td>14.7</td>
<td>56.6</td>
</tr>
<tr>
<td>[(R2N)3P=N–P(N(CH2)6)2]Br+</td>
<td>66</td>
<td>20.1</td>
<td>61.2</td>
</tr>
<tr>
<td>[(Me2N)3P=N–P(NMe2)2]Br+</td>
<td>94</td>
<td>23.5</td>
<td>54.8</td>
</tr>
</tbody>
</table>

a) All spectra were recorded in [D6]MeCN.

Scheme 5. Umpolung by oxidation of (R2N)3P=N–P(NR2)2 (2–4) by reaction with bromine.

A complementary strategy for the preparation of the related P 2-electrophiles [(Me2N)3P=N–P(NMe2)2]Cl+[BF4]– and
[(CH2)4N]3P=N–[(CH2)4]2Cl+[BF4]– from (R2N)3P=N–P(NR2)2 and POCl3 was reported by Schwesinger et al.[11]

Reactivity of (Me2N)3P=N–P(NMe2)2 towards Bis(triflyl)
imide

The preparation of thermally highly stable protic ionic li-
q uids containing protonated superbases like phosphazenes or
guanidines as cations and a bis(triflyl)imide anion was reported by Luo et al.[39] In this context, we obtain a room temperature ionic liquid of low viscosity by direct protonation of \((\text{Me}_2\text{N})_3\text{P} = \text{P} = \text{P} (\text{NMe}_2)_2\) (1) with bis(triflyl)imide (HTFSI) in ethyl ether (Scheme 6). The reaction is accompanied by a high field shift of the PIII signal and a shift of the \(^1J_{\text{PP}}\) coupling constant from 109.1 Hz to 52.4 Hz. The P–H proton exhibits a proton resonance at \(\delta = 6.94\) ppm in \([\text{D}_3]\)MeCN and a strong \(^1J_{\text{PH}}\) coupling constant of 587.4 Hz. Even stronger \(^1J_{\text{PH}}\) coupling constants were reported for \([\text{(Et}_2\text{N})_3\text{P} = \text{H}]^+ [\text{BF}_4]^- \) (630 Hz), \([[(\text{CH}_2)_5\text{N})_3\text{P} = \text{H}]^+ [\text{BF}_4]^- \) (632 Hz)[40] or the unstable \([\text{(Me}_2\text{N})_3\text{P} = \text{H}]^+ [\text{OSO}_2\text{CF}_3]^- \) (680 Hz).[41]

Scheme 6. Reaction (Me_2N)_3P=N–P(NMe_2)_2 (1) with bis(triflyl)imide.

Preparation of P_2-Bisphosphazides

The reaction of the mixed valent P V-PIII species (R_2N)_3P=N–P(NR_2)_2 with 1,8-diazidonaphthalene yielded thermally stable P_2-bisphosphazides in a tandem Staudinger reaction. The reaction follows patterns observed for (Me_2N)_3P=N–P(NMe_2)_2 and [(CH_2)_4N]_3P=N–P[N(CH_2)_4]_2.[9] P_2-TPipPN(2N_2) and P_2-TAzPN(2N_2) were obtained as deep green solids in good yields (Scheme 7, Table 5).

Scheme 7. Preparation of the P_2-bisphosphazides P_2-TPipPN(2N_2) and P_2-TAzPN(2N_2).

Table 5. \(^{31}\text{P} NMR\) spectroscopic data of P_2-bisphosphazides.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield /%</th>
<th>(\delta_p /\text{ppm})</th>
<th>(\delta_h /\text{ppm})</th>
<th>(^1J_{\text{PP}} /\text{Hz})</th>
</tr>
</thead>
<tbody>
<tr>
<td>P_2-TPPPN(2N_2)</td>
<td>68</td>
<td>19.7</td>
<td>9.5</td>
<td>48.0</td>
</tr>
<tr>
<td>P_2-TPipPN(2N_2)</td>
<td>69</td>
<td>20.8</td>
<td>15.1</td>
<td>53.5</td>
</tr>
<tr>
<td>P_2-TAzPN(2N_2)</td>
<td>74</td>
<td>23.0</td>
<td>21.8</td>
<td>57.2</td>
</tr>
<tr>
<td>P_2-HMPN(2N_2)</td>
<td>85</td>
<td>24.0</td>
<td>19.4</td>
<td>51.7</td>
</tr>
</tbody>
</table>


They can be clearly distinguished from corresponding superbasic bisphosphazenes by \(^{13}\text{C} NMR\) spectroscopy, ESI mass spectrometry, elemental analysis and the typical deep green color of the arylidiazophosphorane. Table 5 summarizes spectroscopic data of P_2-TPipPN(2N_2) and P_2-TAzPN(2N_2) and related P_2-bisphosphazides. From all bisphosphazides presented in Table 5, only P_2-TPPPN(2N_2) displayed a thermally or photochemically induced selective N_2 elimination path towards the hyperbasic proton chelating bis-diphosphazene proton sponge P_2-TPPPN.[8]

Structural Investigations

Crystal data and experimental conditions of molecular structures presented in the main manuscript are listed in Table S2 (Supporting Information).

\([(\text{CH}_2)_3\text{N})_3\text{P} = \text{N} = \text{P} (\text{CH}_2)_3\text{N}]_2 \text{HCl} (3\text{-HCl})\]

The compound crystallizes in the orthorhombic space group Pna21 with four molecular units in the unit cell (Figure 3). The P–Cl bonds show slightly different lengths of 2.143(1) and 2.181(1) Å and are longer than observed in amino-substituted reference Me_2N–PCl_2 [P–Cl: 2.091(1), 2.095(1) Å].[42] This fact can be referred of the strongly electron-donating character of the phosphazenyl substituent [(CH_2)_5N]_3P=N– and donation of electron density from the nitrogen atom’s lone pair into the \(\sigma^*-\text{P} = \text{Cl}\) bond. In accord with this negative hyperconjugation model N4-P2 [1.575(3) Å] is very short for a formal P–N single bond, it is even slightly shorter than N4-P1 [1.592(3) Å] which refers to the formal phosphazene P=N bond. The distances between P1 and the three piperidino nitrogen atoms [1.634(2) to 1.646(2) Å] serve as internal standard for a P–N single bond.[43] A valence bond description [N,P^=N=PCl]Cl^– might best describe the trend induced by negative hyperconjugative interaction. As a consequence, a large angle P1–N4–P2 141.0(1)° is observed.[44]
tively. 3-HCl crystallizes in the triclinic space group $P\bar{1}$ with two molecular units in the unit cell (Figure 4). The molecular structure of its hydrochloride proves that the $P^{III}$ atom is the most basic site of [(CH$_2$)$_3$N]$_3$P=N=P[N(CH$_2$)$_2$]$_2$, which was predicted by theory (vide infra). The acidic proton could be located on the Fourier map between basic P2 and Cl2 atoms. The P–H distance of 1.28(3) Å is similar to the corresponding HCl (ellipsoids with 30% probability, carbon bonded hydrogen atoms are omitted for clarity). Selected bond lengths /Å and angles /°: P1–N1 1.630(2), P1–N2 1.592(2), N2–P1 1.638(2), P1–N3 1.640(2), N3–P1 1.584(2), N4–P1 1.576(2), P2–N5 1.622(3), P2–N6 1.632(2), P2–H100 1.28(3), P1–N4–P2 130.1(1). The H100···Cl distance of 2.50(2) Å is below the sum of van der Waals radii (2.85 Å) and indicates a weak interaction between the acidic proton and the chloride anion. The N4–P1 and N4–P2 distances are nearly equal and in the range of P–N double bonds, which suggests a delocalization of the positive charge over the PNP system with the three canonical forms (R$_2$N)$_3$P^-N=P[NR$_2$]$_2$, (R$_2$N)$_3$P=N=P[NR$_2$]$_2$ and (R$_2$N)$_3$P=N=P–H[NR$_2$]$_2$. The P1–N4–P2 angle [130.1(1)°] is smaller than in [(CH$_2$)$_3$N]$_3$P=N–P[N(CH$_2$)$_2$]$_2$ (141.0(1)°). The distances between the phosphorus atoms and the nitrogen atoms of the piperidino groups range from 1.622(3) Å to 1.640(2) Å and are similar to the values found for [(CH$_2$)$_3$N]$_3$P=N–PCl$_2$. 

Figure 4. Molecular structure of [(CH$_2$)$_3$N]$_3$P=N=P[N(CH$_2$)$_2$]+HCl (3·HCl) (ellipsoids with 30% probability, carbon bonded hydrogen atoms are omitted for clarity). Selected bond lengths /Å and angles /°: P1–N1 1.638(2), P1–N2 1.639(2), P1–N3 1.640(2), P1–N4 1.584(2), N4–P1 1.576(2), P2–N5 1.622(3), P2–N6 1.632(2), P2–H100 1.28(3), P1–N4–P2 130.1(1).

The Br···Br distance increases with the electron-donating properties of R$_3$P in the order Ph$_3$P < Et$_3$P < iPr$_3$P < ([(Me$_2$N)$_3$P]=N)(Me$_2$N)$_2$P. The P–Br distance in [(Me$_2$N)$_3$P]=N=P(NMe$_2$)$_2$Br]*Br$^-$ [2.208(1) Å] is longer than observed in the literature-known structures [(Ph$_3$PBr)$^+$Br$^-$: 2.181(3) Å, [Et$_3$PBr]$^+$Br$^-$: 2.173(3) Å, [iPr$_3$PBr]$^+$Br$^-$(CH$_2$Cl)$_2$: 2.185(3) and 2.174(3) Å]. This is a result of the electron rich [(Me$_2$N)$_3$P]=N– substituent donating electron density into the σ$^*$-P–Br bond, which is becoming less attractive for donation of the bromide donor Br$^-$2. As observed for the other two molecular structures discussed herein, the formal double bond P1–N4 [1.592(2) Å] is again longer than N4–P2 [1.551(2) Å].

The Br···Br distance increases with the electron-donating properties of R$_3$P in the order Ph$_3$P < Et$_3$P < iPr$_3$P < ([(Me$_2$N)$_3$P]=N)(Me$_2$N)$_2$P. The P–Br distance in [(Me$_2$N)$_3$P]=N=P(NMe$_2$)$_2$Br]*Br$^-$ [2.208(1) Å] is longer than observed in the literature-known structures [(Ph$_3$PBr)$^+$Br$^-$: 2.181(3) Å, [Et$_3$PBr]$^+$Br$^-$: 2.173(3) Å, [iPr$_3$PBr]$^+$Br$^-$(CH$_2$Cl)$_2$: 2.185(3) and 2.174(3) Å]. This is a result of the electron rich [(Me$_2$N)$_3$P]=N– substituent donating electron density into the σ$^*$-P–Br bond, which is becoming less attractive for donation of the bromide donor Br$^-$2. As observed for the other two molecular structures discussed herein, the formal double bond P1–N4 [1.592(2) Å] is again longer than N4–P2 [1.551(2) Å].

The gas phase proton affinity and gas phase basicity of phosphines 1–4 are calculated employing the ωB97X-D/6-311+G(d,p)/ωB97X-D/6-31+G(d) theoretical model. The validity of this theoretical model is confirmed in a paper of Bachrach, where it was found that the ωB97X-D functional provides more accurate values of gas phase proton affinities and gas basicities of phosphines than M06–2X and/or B3LYP functionals. The pK_BH$^+$ values in acetonitrile are calculated according to the approach of Casasnovas et al. where a full geometry optimization in solution has been performed utilizing the CPCM solvation model. The Schwesinger base $r$Bu-P$_2$(dma)$_5$ (5) with an experimental pK$_{BH}$+(MeCN) value of 33.49, and the phosphine P(CH$_2$)$_3$ with a pK$_{BH}$+(MeCN) value of 15.5 are applied as reference bases giving the corresponding calculated pK$_{BH}$+$^*$, pK$_{BH}$+$^*$+ values. Herein, we will compare the basicity of mono-phosphazeny phosphines 1–4 with Dielmanns tris-(1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidene)-dissopropylphosphine with a calculated pK$_{BH}$+(MeCN) of 38.8. We also include the Verkade base N(CH$_2$CH$_2$NMe)$_2$P (6) into this basicity comparison. Calculated gas phase proton affinities, gas basicities and pK$_{BH}$+$^*$+(MeCN) values are given in Table 6.

Figure 5. Molecular structure of [(Me$_2$N)$_3$P]=N=P(NMe$_2$)$_2$Br]*Br$^-$ (ellipsoids with 30% probability, hydrogen atoms are omitted for clarity). Selected bond lengths /Å and angles /°: P1–N1 1.630(2), P1–N2 1.632(2), P1–N3 1.638(2), P1–N4 1.584(2), N4–P1 1.576(2), P2–N5 1.622(3), P2–N6 1.632(2), P2–H100 1.28(3), P1–N4–P2 130.1(1).
Table 6. The calculated gas phase proton affinities (PA), gas phase basicities (GB), and $pK_{BH}^+$ (MeCN) values of phosphazenyl phosphines 1–4 and reference bases 5–7. Values in square brackets are experimental results taken from the literature[50,51,17].

<table>
<thead>
<tr>
<th>Molecules</th>
<th>PA $p^H$</th>
<th>GB $p^H$</th>
<th>$pK_{BH}^+$ $pK_{BH}^+^{+1}$</th>
<th>$pK_{BH}^+^{+2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Me$_2$N)$_3$P=N-P(NMe$_2$)$_2$</td>
<td>265.8</td>
<td>256.0</td>
<td>257.4</td>
<td>245.7</td>
</tr>
<tr>
<td>[(CH$_2$)$_3$N]$_3$P=P-N[CH$_2$]$_2$</td>
<td>274.7</td>
<td>262.4</td>
<td>267.9</td>
<td>256.1</td>
</tr>
<tr>
<td>[(CH$_2$)$_3$N]$_3$P=P-N[CH$_2$]$_2$</td>
<td>272.4</td>
<td>259.4</td>
<td>265.4</td>
<td>251.5</td>
</tr>
<tr>
<td>[(CH$_2$)$_3$N]$_3$P=P-N[CH$_2$]$_2$</td>
<td>273.6</td>
<td>259.2</td>
<td>267.7</td>
<td>251.8</td>
</tr>
<tr>
<td>$\text{Bu}_2$P$_2$(dma)$_3$ (5)</td>
<td>–</td>
<td>277.2</td>
<td>–</td>
<td>269.3</td>
</tr>
<tr>
<td>Verkade-Me base (6)</td>
<td>263.1</td>
<td>–</td>
<td>256.0 [260.8]</td>
<td>–</td>
</tr>
<tr>
<td>P(CH$_3$)$_3$ (7)</td>
<td>230.9</td>
<td>–</td>
<td>226.4 [221.4]</td>
<td>–</td>
</tr>
</tbody>
</table>

- a) Reference[50].
- b) Reference[51].
- c) Reference[17].
- d) Values denoted by PIII are PA and GB values for protonation at the phosphorus atom, whereas (=N–) represent the values for protonation at the imine nitrogen atom. $pK_{BH}^+$, $pK_{BH}^+^{+1}$, and $pK_{BH}^+^{+2}$ are calculated utilizing $\text{Bu}_2$P$_2$(dma)$_3$ and P(CH$_3$)$_3$, as a reference bases, respectively.

Perusal of the data presented in Table 6 reveals that the most basic protonation site of the P$_2$ bases 1–4 is the phosphorus atom and not the phosphazeny nitrogen atom (Scheme 8). Proton affinities for protonation at phosphorus are denoted by PA ($p^H$) whereas PAs where the imine nitrogen atom is protonated are denoted by PA (=N–). Protonation on the imine nitrogen atom gives PA values lower by 9.8–14.4 kcal·mol$^{-1}$ than obtained for the protonation on the phosphorus atom. It appears that the calculated gas phase proton affinities and gas phase basicities of all investigated P$_2$ phosphines (1–4) exceed that of the paradigmatic Verkade proazaphosphatran base N(CH$_2$CH$_2$NMe)$_3$P (6). However, it should be noticed that the experimental and computational gas phase basicity for the Verkade base differs substantially (4.8 kcal·mol$^{-1}$). The difference is even larger if the B3LYP functional is employed. According to the B3LYP/6-311+G(2df,p)/B3LYP/6-31G(d) theoretical model, the PA and GB values of 6 are 261.0 and 252.8 kcal·mol$^{-1}$,[18] M062X/6-31+G(2df,p)/M062X/6-31G(d) gives by far the largest discrepancy compared to the experimental data, since the calculated PA and GB values obtained by this functional are 257.2 and 249.5 kcal·mol$^{-1}$, respectively. Therefore, although 2–4 are more basic than 6 in the gas phase, their $pK_{BH}^+$ values in acetonitrile are lower. The lower $\Delta G_{sol}$ could be rationalized by a steric hindrance of the phosphorus atom due to the bulkiness of the (R$_2$N)$_3$P=N– substituents in the case of 1–4 which prevents the access of the solvent molecules to the protonated phosphorus atom. In the Verkade base 6 this is not the case and the protonated phosphorus atom is more exposed to the solvent.

![Scheme 8. Optimized gas phase structures of (Me$_2$N)$_3$P=N-P(NMe$_2$)$_2$ and (Me$_2$N)$_3$P=P-(NMe$_2$)$_2$H$^+$](image-url)

According to the calculations, (Me$_2$N)$_3$P=N-P(NMe$_2$)$_2$, [(CH$_2$)$_3$N]$_3$P=P-N[CH$_2$]$_2$ and [(CH$_2$)$_3$N]$_3$P=P-N[CH$_2$]$_2$ exhibit by several order of magnitude higher $pK_{BH}^+$ values on the acetonitrile scale than the
corresponding secondary amines dimethylamine, piperidine or azepane with experimentally measured $pK_{BH^+}$ values around 19.\cite{55} Since the basicity difference between the studied $P_2$ species and the corresponding secondary amines is relatively high in the gas phase and in acetonitrile solution, possible differences in crystal lattice energy, in Gibbs energy of solvation of ions, and in energy of ion pair formation in solution are responsible for the success of above mentioned syntheses applying amines as base and nucleophile.

### Donor Strength of mono-PAPs

The donor strength of an electron donor depends on the nature of the acceptor. In this study, the electron-donor capabilities of selected mono-PAP \((dma)_3P=N–P(dma)_2\) (1) and \((Pyr)P=N–P(Pyr)\) (2) (dma = dimethylamino, Pyr = pyrrolidino) were quantified by their Tolman electronic parameters (TEPs)\cite{56} and their $^1J_{PSe}$ coupling constants\cite{37} applying the same reference acceptors, \([Ni(CO)_3]\) and \([Se]\), used in scaling up our tris-PAP \([(dma)_3P=N][PSe]_3\) and \([(Pyr)_3P=N][PSe]_3\) (Table 7).\cite{24}

**Table 7.** Donor capability measured as TEP a) of $[L-Ni(CO)_3]$ complexes and as $^1J_{PSe}$ constants of selenides of mono-PAP 1 and 2 and references Verkade-Me base and tris-PAP.

<table>
<thead>
<tr>
<th>TEP /cm$^{-1}$ a)</th>
<th>$^1J_{PSe}$/Hz b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(dma)_3P=N–P(dma)_2] (1)</td>
<td>2047.4</td>
</tr>
<tr>
<td>[(Pyr)P=N–P(Pyr)] (2)</td>
<td>2042.4</td>
</tr>
<tr>
<td>Verkade-Me base</td>
<td>2057.0</td>
</tr>
<tr>
<td>([(dma)_3P=N][PSe]_3)</td>
<td>2022.4</td>
</tr>
<tr>
<td>([(Pyr)_3P=N][PSe]_3)</td>
<td>2018.6</td>
</tr>
</tbody>
</table>


For this purpose, 1 and 2 were reacted with \([Ni(CO)_3]\) and with grey selenium. Corresponding adducts \([Ni(PSe)_3][Ni(CO)_3]\), \([Ni(PSe)_3][Ni(CO)_3]\) as well as \([Se][Se]\) and \([Se][Se]\) were isolated and characterized. The higher the P-donor strength, the lower the TEP value, the frequency of the A1 C-O stretching mode, and the lower the $^1J_{PSe}$ coupling constant of their P-selenides.

On the TEP scale, the donor strength of the mono-PAP 1 and 2 is superior to that of Verkade-Me base.\cite{58,59} It is in the range of 2050$\pm$5 cm$^{-1}$ characteristic for classical NHCs or even stronger. On the NMR scale of corresponding selenides, the donor strength of Verkade-Me base is in between 1 and 2, interestingly a similar trend as found in basicity. As expected mono-PAP do not keep up with the unrivaled donor strength of tris-PAP.

### Conclusions

After having presented superbasic $P_2$-phosphazene chelates in previous publications, we shed light onto their mono-phosphazenyolphosphine $P_2$-precursors within this work allowing insight into their facile and scalable synthesis, reactivity, spectroscopic properties, structural features, their basicity in solution and the gas phase, their nucleophilicity and donor strength. We are convinced that the amino-substituted $P_2$-nu-

### Experimental Section

Reactions were carried out under inert atmosphere using standard Schlenk techniques. Moisture and air sensitive substances were stored in a conventional nitrogen-flushed glovebox. Solvents were purified according to literature procedures and kept under an inert atmosphere. Phosphorus trichloride was distilled prior to use. Pyrrolidine, piperidine and azepane were stirred over CaH$_2$ overnight and distilled prior to use. $P(N(CH_2)_{8})_3$ was prepared by the reaction of $PCl_3$ with pyrrolidine in THF on the basis of a publication by Dellinger et al.\cite{60} $P(N(CH_2)_{8})_3$ was obtained in a similar procedure in ethyl ether, but purification was performed by precipitation from acetone instead of distillation.\cite{61} $P(N(CH_2)_{8})_3$ was prepared via a transamination reaction of $P(NEt_2)_3$ with azepane.\cite{62} Synthetic procedures of all new compounds and optimized ones of literature known $[(Me_2N)_3P=N–P(NMe_2)Br]^(+)[Br]^{-}$, $[(CH_2)_3N]P=N–P(N(CH_3)_{2})Br]^(+)[Br]^{-}$, and their corresponding precursors are presented in the Supporting Information.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the deposition numbers CCDC-977140, CCDC-1955666, and CCDC-1955687. (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

### Supporting Information

(see footnote on the first page of this article): This includes synthetic procedures, NMR protonation experiments, NMR and IR spectra, crystallographic information and computational details.

### Acknowledgements

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