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Phosphorus-Containing Superbases: Recent Progress in the Chemistry of Electron-Abundant Phosphines and Phosphazenes

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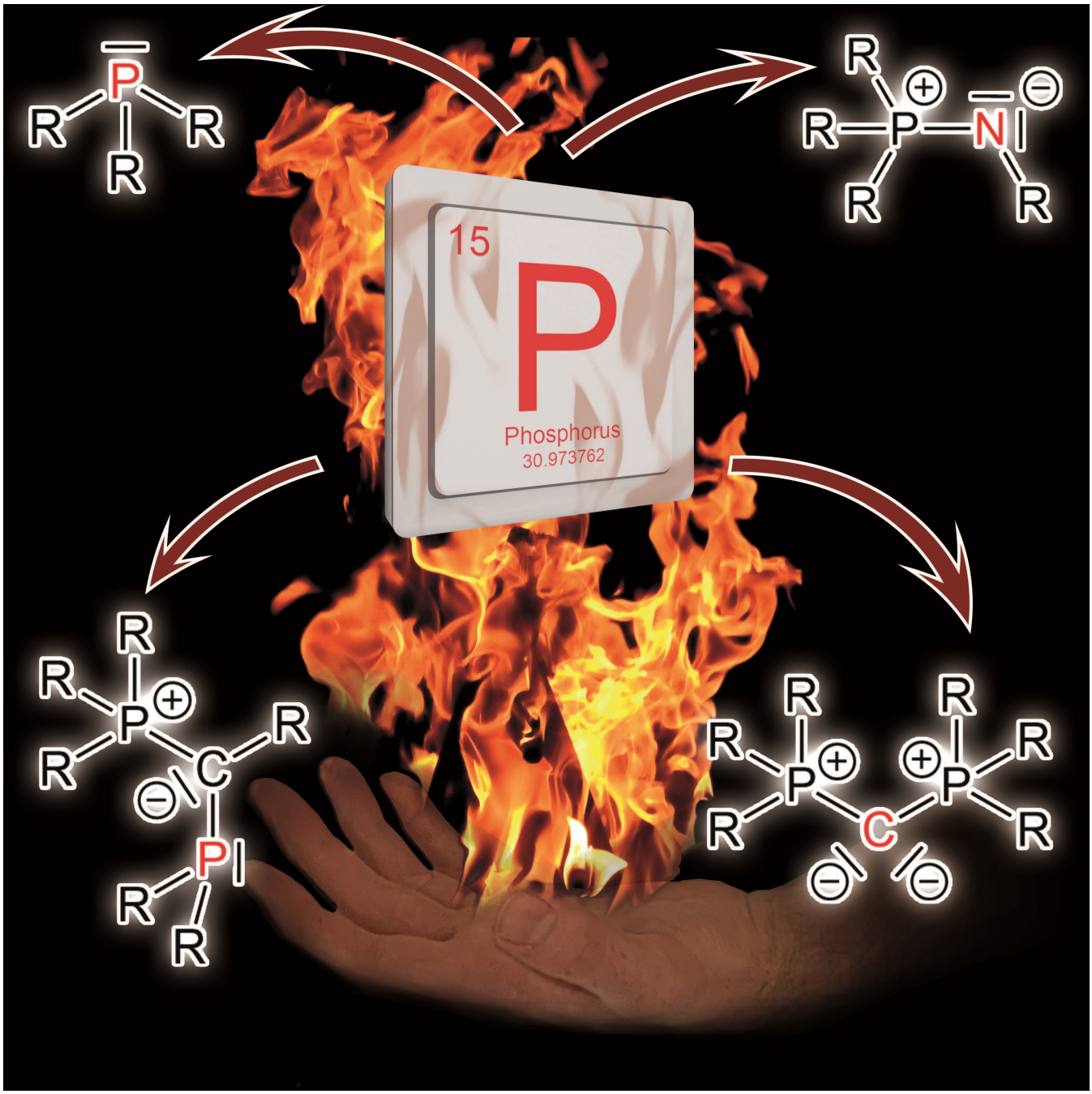

Abstract: The renaissance of Brønsted superbases is primarily based on their pronounced capacity for a large variety of chemical transformations under mild reaction conditions. Four major set screws are available for the selective tuning of the basicity: the nature of the basic center (N, P, …), the degree of electron donation by substituents to the central atom, the possibility of charge delocalization, and the energy gain by hydrogen bonding. Within the past decades, a plethora of neutral electron-rich phosphine and phosphazene bases have appeared in the literature. Their outstanding properties and advantages over inorganic or charged bases have now made them indispensable as auxiliary bases in deprotonation processes. Herein, an update of the chemistry of basic phosphines and phosphazenes is given. In addition, due to widespread interest, their use in catalysis or as ligands in coordination chemistry is highlighted.

1. Introduction

This minireview discusses the recent progress of the chemistry of selected uncharged electron-abundant phosphines and phosphazenes within the past five years. Their broad applicability as Brønsted superbases or as Lewis basic ligands made them flourish to highly important tools in organic and inorganic chemistry and indispensable in catalytic chemistry.[1]

The term *superbase* is not unambiguously settled in the literature and is used rather arbitrarily for extremely strong organic or inorganic bases capable of abstracting a proton. Caubère[2] and Schlosser[3] defined superbases as the combination of two or more different metal bases leading to mixtures with new properties. In organic chemistry in particular, however, it has become common to compare nonionic bases with regard to their thermodynamic and kinetic properties in deprotonation reactions. Typically, Alder's proton sponge 1,8-bis(dimethylamino)naphthalene serves as the reference point.[1,4,5]

The lone pair of electrons at the phosphorus atom in phosphines PR_3 marks them out as Lewis bases. The substituents R on the phosphorus atom strongly govern its donor capability as is obvious by the comparison of calculated ionization potentials IP_v and electron affinities EA_v of tris(trifluoromethyl)phosphine and trimethylphosphine (Figure 1). While electron-donating groups evoke energetically increased HOMO-LUMO levels accompanied by an increased donor strength and basicity, electron-withdrawing groups stabilize the HOMO and LUMO significantly and thus decrease the donation ability and basicity of those species.[6]

It is well known that electron-poor phosphines as weakly Lewis basic ligands form electron-deficient transition metal complexes.[8,9,10,11] The devise of phosphines with stronger σ-donating properties is of growing interest, since N-heterocyclic carbenes (NHC) as strong σ-donor ligands have already surpassed the donor capability of simple alkylphosphines.[9,12]

Tris(pyrrolidinyl)phosphine exhibits similar ligating properties as tri-*n*-butyl-phosphine, which can be explained by π-donation of free lone pairs of the nitrogen atoms.[13] Counterintuitively, the exchange of one π-donating but σ-electron-withdrawing amino substituent by one alkyl group affords the corresponding more Lewis basic bis(pyrrolidinyl) alkylphosphines, featuring similar donor properties as tri-*tert*-butylphosphine.[14] Thus it is obvious that an increased basicity and overall donor strength is achieved by the implementation of strongly π-donating N-based functionalities that are able to compensate the electron-withdrawing effect of the contact nitrogen atoms.

This concept may also be applied for the design of phosphazenes (phosphanimines) of the type $R_3P{=}NR'$. In this case protonation and metal-coordination occurs at the nitrogen atom of the imino group, which represents the Lewis basic center. The overall donor capacity of the nitrogen lone pair is improved by π-donating amino substituents on the phosphorus atom, which also mitigate the positive charges at the phosphorus centers engendered by protonation or coordination.[5,15,16]

In addition to the pK_{BH^+} value, the proton affinity as well as the gas-phase basicity of phosphazenes and phosphines have typically been chosen as a qualitative measure for their Brønsted basicity and overall σ-electron-donation ability, respectively.[5,17,18,19] The Tolman electronic parameter (TEP) is also a simple and thus broadly applied instrument to quantify the electronic properties of tailor-made ligands.[8] However, it should be kept in mind, that the TEP is not a qualitative measure for the σ-donor strength itself, but is a sum of both σ-donation and π-backbonding.

In the following we will highlight modern superbase design and will also discuss important applications. First of all, we will

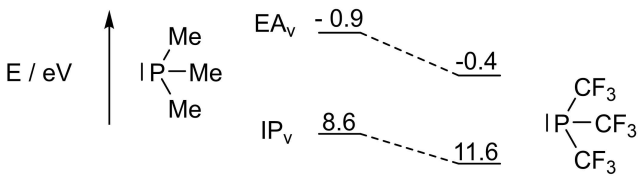

Figure 1. Ionization potential (IP_v) and electron affinity (EA_v) of trimethylphosphine and tris(trifluoromethyl)phosphine (B3LYP/6-311 + G(d,p)).[6,7]

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briefly mention historical milestones in the development of phosphazene and phosphine compounds with strong donor substituents.

The roots of phosphazene chemistry date back to the year 1919, when Staudinger presented the first iminophosphoranes **1**, which were obtained by the reaction of triorganophosphines with organic azides (Scheme 1).[20] Most commonly, the transiently formed phosphazides evade isolation and suffer from liberation of N_2.

The protocol of Staudinger represents the most efficient and nowadays preferably used pathway to a variety of iminophosphoranes.[21,22,23,24] However, it should be kept in mind that the use of sensitive azides is always hazardous due to violent decompositions[25] which is particularly true for hydrazoic acid (HN_3).

The strategy presented by Kirsanov in 1950 utilizes a halogenotriorganophosphonium halide which is converted to the corresponding iminophosphoranes **1** by primary amines (Scheme 1).[26] This method circumvents the need of dangerous and possibly non-existent azides, delivering products in high yields.

A few years later in 1959, Appel et al. succeeded in the isolation of the first iminophosphorane $Ph_3P{=}NH$ (**2a**) by the deprotonation of the corresponding iminium halide with sodium amide in liquid ammonia.[27,28] Iminophosphoranes **2** of the general formula $R_3P{=}NH$ are accessible by the reaction of phosphines with chloramines.[28,29] Another convenient method for the synthesis of **2** was developed by Birkofer in 1964 through Staudinger reactions of phosphines with trimethylsilylazide and the subsequent acid catalyzed hydrolysis of initially obtained trimethylsilyl iminophosphoranes **3** in methanol (Scheme 1).[23,30] The reaction of phosphines with hydrazoic acid and the subsequent reaction with sodium in liquid ammonia is also described.[31]

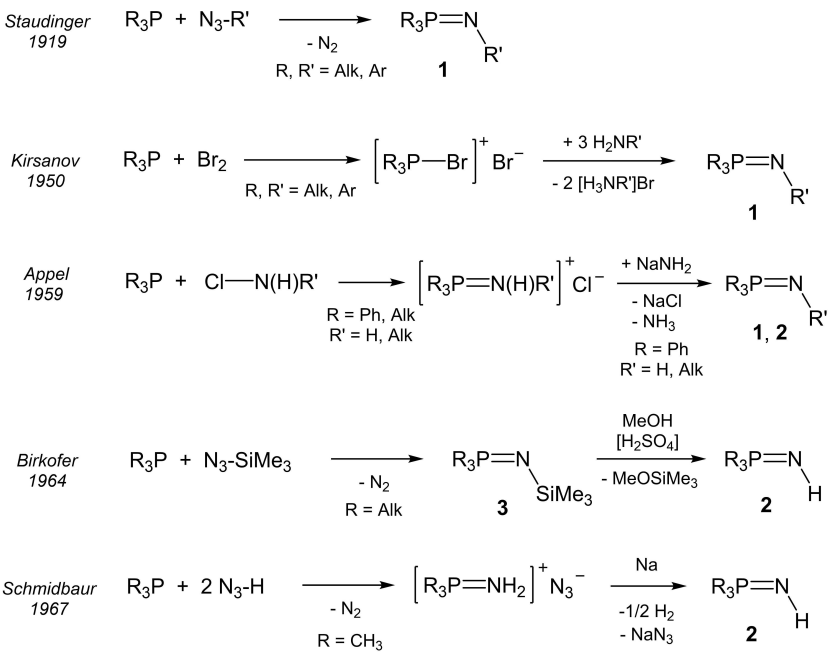
The availability of iminophosphoranes **2** has opened the door to a rich chemistry, for example, the formation of metalorganic iminophosphoranes **4** and **6** resulting from deprotonation of **2** with organolithium bases[31–33] (Scheme 2) or from adducts **5** with organometallic compounds among others ($AlMe_3$, $GaMe_3$, $ZnMe_2$, …).[31,33,34] In order to study electron-abundant iminophosphoranes, Issleib et al. decided to incorporate electron-donating dimethylamino groups at the phosphorus atom in **2**.[35] The syntheses of the mono- to tris (dimethylamino) derivatives were performed according to the procedure by Appel et al. (Schemes 1 and 2) through the reaction of phosphines with chloramines and subsequent deprotonation.[27–29] This series was completed by Goubeau et al. in 1974 with the tetrakis(dimethylamino)phosphonium ion.[21] Two years later in 1976, Schmutzler et al. further explored properties of (dimethylamino)iminophosphoranes **3** and reported on the first entirely dialkylamino substituted diphosphazene $(Me_2N)_3P{=}N{-}P(NMe_2)_2{=}N{-}SiMe_3$ (**7**, Scheme 2).[24]

Phosphazenylphosphines **8** as early examples of electron-rich phosphines were first described by Schmidbaur in 1968.[33] Their syntheses are based upon the reaction of lithium imino (trialkyl)phosphoranes **4** with chloro(dialkyl)phosphines (Scheme 3)[33] but also proceed by transmetalation of **3** with chlorophosphines.[36] Due to the high electron density at the tricoordinate phosphorus atom in **8**, alkylation of phosphazenylphosphines with alkylhalides is facile and affords bis (trialkylphosphine)iminium salts (**9**, Scheme 3).[36] These cations show a high thermal stability and moreover are resistant towards acids and bases.[37] Consistently, representatives like bis (triphenylphosphine)iminium (PNP^+) salts, first prepared by Appel et al.[37] in 1961, are frequently applied as appropriate cation sources in the stabilization and crystallization of salts featuring reactive anions.[38]

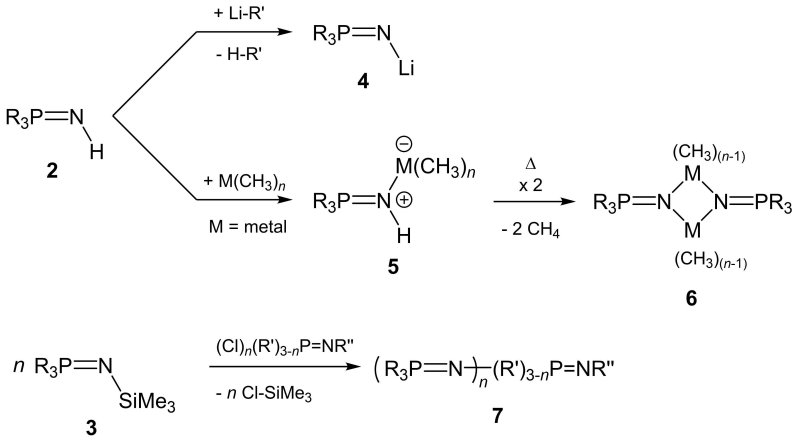
More than three decades after Staudinger's seminal synthesis of the isoelectronic phosphonium methanides or methylene phosphoranes **10** in 1919,[39] Wittig discovered their utility as reactants in a carbonyl-olefination process when brought in contact with aldehydes and ketones.[40] The so-called Wittig reaction remains one of the most important methods in olefin syntheses.[41] Through deprotonation and conversion with chlorophosphines, Issleib and co-workers succeeded in the functionalization of **10** and reported on first examples of C-phosphino methylene phosphoranes or ylidylphosphines **11** (YPhos, $Ph_3P{=}C(R){-}PR'_2$, Scheme 3),[42] of which numerous representatives are known by today.[43] In stark contrast to the reactivity of **8** towards alkylhalides, alkylation of ylidylphosphines **11** occurs at the central carbon atom, resulting in salt-like phosphinomethyl phosphonium halides **12** (Scheme 3). This behavior is rationalized by the high negative charge density at the carbon atom expressed by a zwitterionic resonance structure.[44–46] Investigations on diphosphinomethane[47] and diphosphinomethanides[48] are also relevant in this context.

Robin F. Weitkamp earned his M.Sc. degree from Bielefeld University in 2018 under the supervision of Berthold Hoge and received his Ph.D. in inorganic chemistry, also with Hoge, in 2021. His academic research is focused on the investigation of highly nucleophilic and strongly reducing naked anions, which can be prepared by deprotonation reactions with phosphazene bases, and thus allow insights into structure–reactivity correlations. Naked anions find practical application in chemical catalysis or SF_6 degradation, among others.

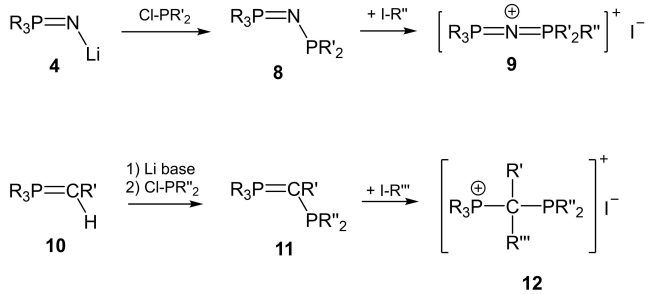
Berthold Hoge received his Ph.D. in inorganic chemistry at Wuppertal University (Germany) with R. Eujen in 1997. After postdoctoral work with K. O. Christe at the University of Southern California (USA) in 1998, he started his habilitation mentored by D. Naumann at the University of Cologne (Germany), which he completed in 2004. He was promoted to Professor of Inorganic Chemistry at the Bielefeld University (Germany) in 2009, with a focus on molecular chemistry containing fluorine, phosphorus and silicon.



Scheme 1. Preparation of iminophosphoranes.



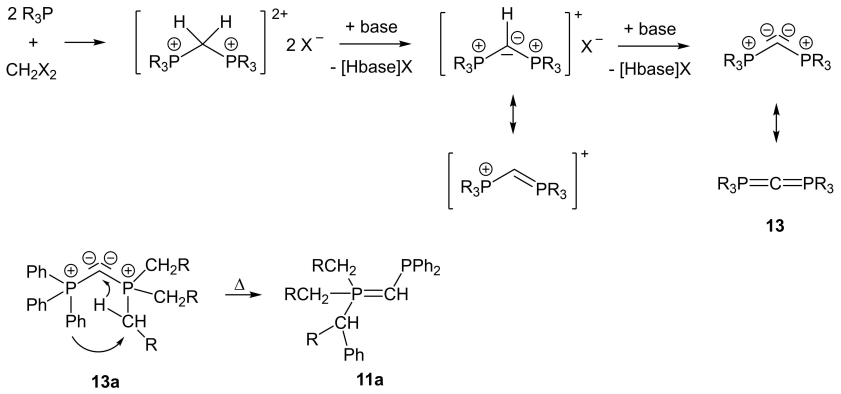
Scheme 2. Selected reactions of iminophosphoranes and functionalization possibilities.



Scheme 3. Comparison of phosphazenylphosphines and phosphinealkylenephosphines.

Carbodiphosphoranes of the general formula $R_3P{=}C{=}PR_3$ (**13**) are isoelectronic to iminiumdiphosphorane cations **9** (Scheme 4).

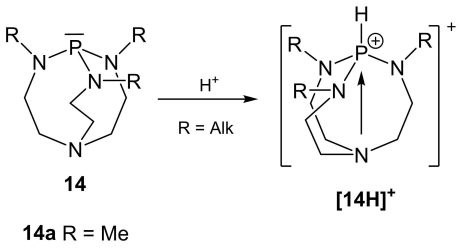
The first symmetric perphenylated carbodiphosphorane $Ph_3P{=}C{=}PPh_3$ was synthesized by Ramirez et al. in 1961,[49] and was followed by asymmetric examples by Appel in 1978.[50] Due to ylid-ylene resonance structures, carbodiphosphoranes **13** can formally be regarded as bisylides with a twofold negative charge at the central carbon atom (Scheme 4). Consequently they act as strong carbon bases in a twofold protonation process towards Brønsted acids.[49,50] The negative charge at the carbon atom of **13** was demonstrated by their capability to function as bridging four-electron ligands in coordination chemistry.[51,52] At higher temperatures carbodiphosphoranes



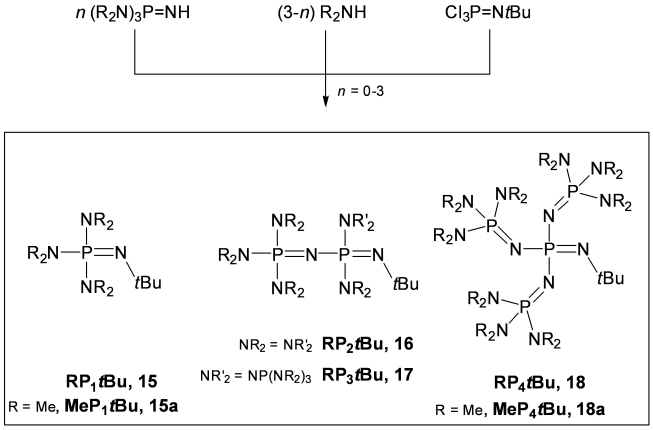
Scheme 4. Preparation of carbodiphosphorane and comparison with iminiumdiphosphorane.

such as **13a** with α-CH units may rearrange under formation of ylidylphosphines **11a** (Scheme 4).[50]

Verkade and co-workers have discovered another important group of Brønsted superbasic electron-rich phosphines, denoted "Verkade bases" (**14**). During their investigation of pentacoordinated phosphatranes of the general formula $[HP(XCH_2CH_2)_3N]^+$ (X = O, NMe) with tricyclic aminetriol[53,54] and triaminoamine[55,56] substituents (Scheme 5), they revealed unusually robust P–H bonds. The remarkably high proton affinity of **14** is caused by a stabilizing electron pair donation of the central nitrogen atom to the cationic center within the tricyclic substituent (Scheme 5), which was also subject of theoretical calculations.[57]



Scheme 5. "Verkade bases" **14**.

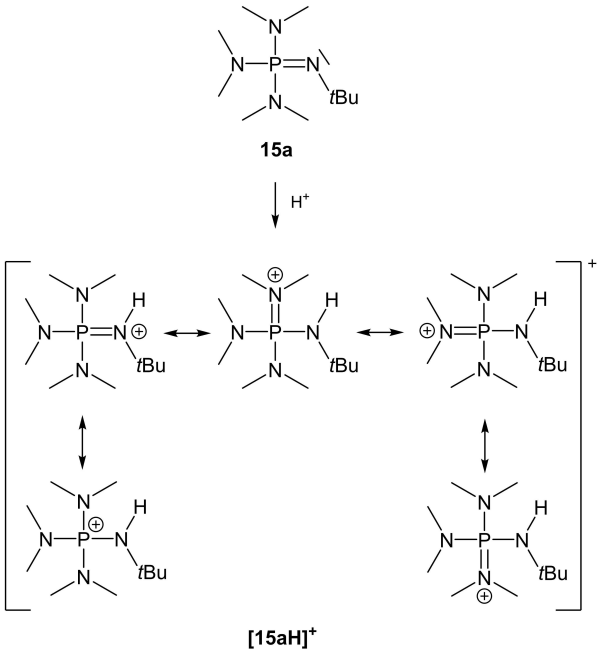


Scheme 6. Preparation of Schwesinger bases.

Oxaphosphatranes resist clean deprotonation due to the large tendency of the anticipated free base towards polymerization.[58] The corresponding highly stable pro-azaphosphatranes **14** ("Verkade bases") are smoothly liberated with KO*t*Bu.[56,58,59,60] With a $^{MeCN}pK_{BH^+}$ value of 32.9 for the methyl derivative **14a**, pro-azaphosphatranes are of similar basicity as diphosphazenes $(R_2N)_3P{=}N\text{-}(R_2N)_2P{=}Nt$Bu (**16**, Scheme 6),[60–62] which were published a few years later by Schwesinger. The phosphines of Verkade type are useful reagents in organic syntheses[63] and enable a large bandwidth of reactions under mild reaction conditions and acts as Lewis base catalyst for the trimerization of isocyanates to isocyanurates[64] or as Brønsted base for syntheses of important oxazoles and pyrroles,[65] as well as for monoalkylations[66] and dehydrohalogenation reactions.[67,68] Pro-azaphosphatranes have also found application as auxiliary bases in Michael addition[69] or 1,2-addition reactions.[70]

Later, when Schwesinger's activities were focused on the preparation and investigation of strong bases with vinamidine structure as auxiliary bases in dehydrohalogenation reactions,[4,71,72] he observed the outstanding proton-accepting properties of amino-substituted phosphanimines and laid the foundation stone of the wide field of the so called "Schwesinger bases".[15,16,62,73,74,75] High thermal stability, reluctance towards oxygen and base hydrolysis,[75,76,77] as well as their easy accessibility on large scales were crucial for their great success in synthetic chemistry.

Phosphazene bases exhibit extremely high $^{MeCN}pK_{BH^+}$ values, which range from 26.9[16,74] for monophosphazene $(Me_2N)_3P{=}Nt$Bu (MeP_1tBu, **15a**) up to 42.7[62] for tetraphosphazene $[(Me_2N)_3P{=}N]_3P{=}Nt$Bu (MeP_4tBu, **18a**; Scheme 6). As previously described, the Brønsted superbasicity of phosphazenes is due to π-donating phosphazenyl- or dialkylamino substituents bonded at phosphorus, which further allows an excellent delocalization of the engendered positive charge of the cations.[16] This is illustrated by the resonance structures of the protonated permethyl monophosphazene base $[MeP_1t$BuH$]^+$ ([**15a**H]$^+$) in Scheme 7.



Scheme 7. Resonance structures of $[MeP_1tBuH]^+$ ($[\mathbf{15a}H]^+$).

The further "homologization" to penta- and heptaphosphazenes results in an only marginal increase in basicity and for the latter in a drastically sensitivity towards acids and air.[62]

The bulky phosphazene homologues **18** combine high Brønsted basicity with low nucleophilicity,[4,15,16,62,71,72] which recommends their versatile employment in dehydrohalogenation reactions,[16,62] biaryl ether couplings[78] and alkylation reactions[1] among others.[56,79]

The Brønsted basicity comparison of Verkade's phosphine $N(CH_2CH_2NMe)_3P$ **14a** with the analogous tricyclic Verkade's iminophosphorane $N(CH_2CH_2NMe)_3P{=}NR$ and the acyclic iminophosphorane $(Me_2N)_3P{=}NR$ **15** revealed the highest basicity for the phosphine within the row: $N(CH_2CH_2NMe)_3P > N(CH_2CH_2NMe)_3P{=}NR > (Me_2N)_3P{=}NR$.[80] Moreover, the cyclic imine derivative is more basic than the acyclic compound. Although Verkade's bases **14** are capable in dehydrohalogenation reactions of secondary and tertiary alkyl halides,[67,68] a pronounced nucleophilicity of this base leads to alkylation with primary alkyl halides as well as an eager formation of coordination adducts with Lewis acids.[54,58,64,81] The good accessibility of the phosphorus atoms of the free bases also applies to the PH functions of the respective protonated forms, which suggests that Verkade's bases **14** cannot be employed for the realization of non-coordinated or "naked" anions. Alkylamino saturated phosphazenium ions offer themselves for the investigation of naked anions, like the naked fluoride anion.[77,82] However, salt metathesis reactions are required, which are often accompanied by poor solubilities or solvent removal issues. Encumbered phosphazene bases like **18** (Scheme 6) can take remedial action. Since neutral phosphazenes can be handled in common nonacidic and nonpolar solvents, deprotonation of even weak acids affords the corresponding highly reactive non-coordinated anions.[83] Due to the central location of the accepted proton in a sterically shielded molecule pocket, coordination and a dynamic proton exchange are hampered.

2. Recent Results and Discussions

2.1. Electron-rich phosphines

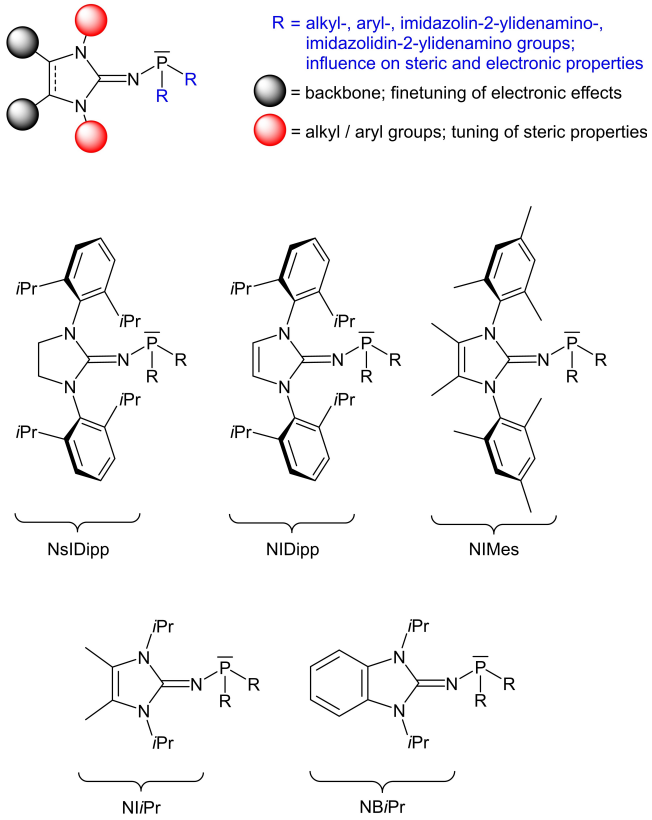
Electron-rich phosphines are available with a variety of different substituents.[8] They play a paramount role as ligands in transition metal catalysis[14,84] and their syntheses are increasingly supported by computational predictions.[85] Their development in recent decades has been accompanied by an impressive variety of commercially available phosphines for nearly every desired demand. Profound discussion, however, would go beyond the scope of this mini review. Thus, in the following chapters we will focus on recent achievements to phosphines of Dielmann, Sundermeyer and Gessner carrying strongly electron-donating imidazoline-2-ylidenamino, pyridinylidenamino, phosphazenyl and ylidyl groups.

2.1.1. Mono and bidentate Imidazolin-2-ylidenamino phosphines (IAPs)

Dielmann and co-workers obtain electron-rich phosphines by employment of strongly π-donating imidazolidine-2-ylidenamino or imidazoline-2-ylidenamino substituents (Scheme 8).[9,86]

Imidazolidine-2-ylidenamino groups already excelled in syntheses of exotic donor free phosphinonitrene[89] and iminophosphonium cations[90] by lowering the electrophilicity at the phosphorus atom. Advantageously, the incorporated NHC backbones have been broadly investigated, and thus enable efficient and easy tuning of steric and electronic properties (Scheme 8). The established syntheses of IAPs are depicted in Scheme 9. The NHC backbones are built up by starting from imidazolium and imidazolidinium salts followed by the subsequent deprotonation with KO*t*Bu prior to conversion in a Staudinger reaction with trimethylsilylazide.[9,86–88,91] Established high-yield syntheses (*i*Pr > 99%, *t*Bu 56%) of dialkyl-IAPs **19a–c**, **20** and **21a–b** proceed by transmetalation of TMS-imidazolin-2-ylidenamines with R_2PCl or in case of $P(NIMes)_2(iPr)$ (**19c**) with PCl_3 and subsequent alkylation with *i*PrMgCl (Scheme 9).[9]

The NI*i*Pr groups are introduced via the free imine as building block, which can be furnished by hydrolysis of the corresponding TMS-compound in methanol.[92] Deprotonation of H-NI*i*Pr with *n*BuLi and conversion with $(iPr)_2PCl$ and $iPrPCl_2$ affords mono- and bis-substituted IAPs **22a** and **22b**, respectively, in high yields of over 87%. However, the tris-compound of **22c** is isolated as the stable adduct $P(NIiPr)_3{\cdot}LiCl$ due to the presence of intermediary formed LiCl from the reaction with PCl_3. LiCl may be separated by heating to 130 °C in *n*-hexane, which affords free $P(NIiPr)_3$ (**22c**) in a 34% yield. In a more convenient route the respective imine itself is employed as the base and used in a quantitative manner (Scheme 9).[86,93]



Scheme 8. IAPs of Dielmann et al.[9,86–88]

However, while (NI*i*Pr)(*i*Pr)$_2$P (**22 a**) is easily liberated, H-NI*i*Pr is not sufficient for the deprotonation of [H–P(NI*i*Pr)$_2$(*i*Pr)]Cl ([**22b**H]Cl) and [H–P(NI*i*Pr)$_3$]Cl ([**22c**H]Cl), thus deprotonation of these compounds is accomplished with KO*t*Bu and delivers the desired phosphines in high yields (> 89 %).[86]

Compound P(NI*i*Pr)$_3$ (22c) represents the strongest Brønsted base within investigated IAPs with an experimental $^{THF}pK_{BH^+}$ value of 31.0 ($^{MeCN}pK_{BH^+}$ = 38.8).[86]

Benzimidazoline-IAPs 23a-e are viable in yields of over 84 % via lithiation of H-NB*i*Pr and subsequent reaction with the respective chlorophosphines.[9,87] Interestingly, employing this strategy P(NB*i*Pr)$_3$ (23e) is accessible without incorporation of LiCl, for which the stronger electron releasing character of NI*i*Pr-groups relative to NB*i*Pr may be responsible.

Electron-rich and strongly Lewis basic IAPs have found application in the activation of small molecules as the most potent and chemically rather inert SF_6 molecule (Scheme 9)[96,97] as well as CO_2[86,87] and SO_2,[98] and they readily form complexes with transition metals,[9,86–88,93] which exhibit outstanding catalytic activities in Suzuki-Miyaura cross-couplings and hydroamination reactions. Moreover, they were employed in FLP systems for the polymerization of methyl methacrylate.[99]

The π-donating power of NI*i*Pr-groups does not only remarkably increase the Lewis and Brønsted basicity at the phosphorus atom, but also evokes an increased hydridic character of the PH unit in [H–P(NI*i*Pr)$_3$]$^+$ ([22cH]$^+$). A salt exchange reaction with NaX (X = $B(C_6F_5)_4^-$ or $BAr^F{}_4^-$) and the subsequent hydrid abstraction affords the first phosphorus dication [P(NI*i*Pr)$_3$][X]$_2$ (Scheme 9).[95]

Chelating IAPs 24–26 were also synthesized by the Dielmann group, whereas the phosphine moieties were either connected via a ferrocene,[9] a 1,3-bis(imidazolin-2-ylidenamino) propylene or a phenylene backbone (Scheme 10).[94] The 1,3-bis (imidazolin-2-ylidenamino)propylene group is built up from the respective dicarbene followed by the reaction with N_2O and hydrochloric acid. The desired product was isolated in a 93 % yield after deprotonation and the subsequent addition of PCl (*i*Pr)$_2$.[94]

The ferrocene backbone is easily incorporated by the reaction of H-NB*i*Pr with a lithium base and the subsequent addition of bis(dichlorophosphino)ferrocene by which diphosphine 26 is isolated in a 81 % yield.[9] In contrast to that, and most likely due to steric repulsion, the analogous reaction of bis (dichlorophosphino)benzene with H-NI*i*Pr as the base and nucleophile solely afforded the chloro-tris(NI*i*Pr) intermediate. All attempts to substitute the chlorine atom by an additional NI*i*Pr group remained challenging and thus substitution by a *tert*-butoxide moiety was performed instead to obtain the diphosphine 25.

All bidentate phosphine ligands were successfully employed for the generation of electron-rich gold(I), palladium(II) and nickel(0) chelate complexes.[94]

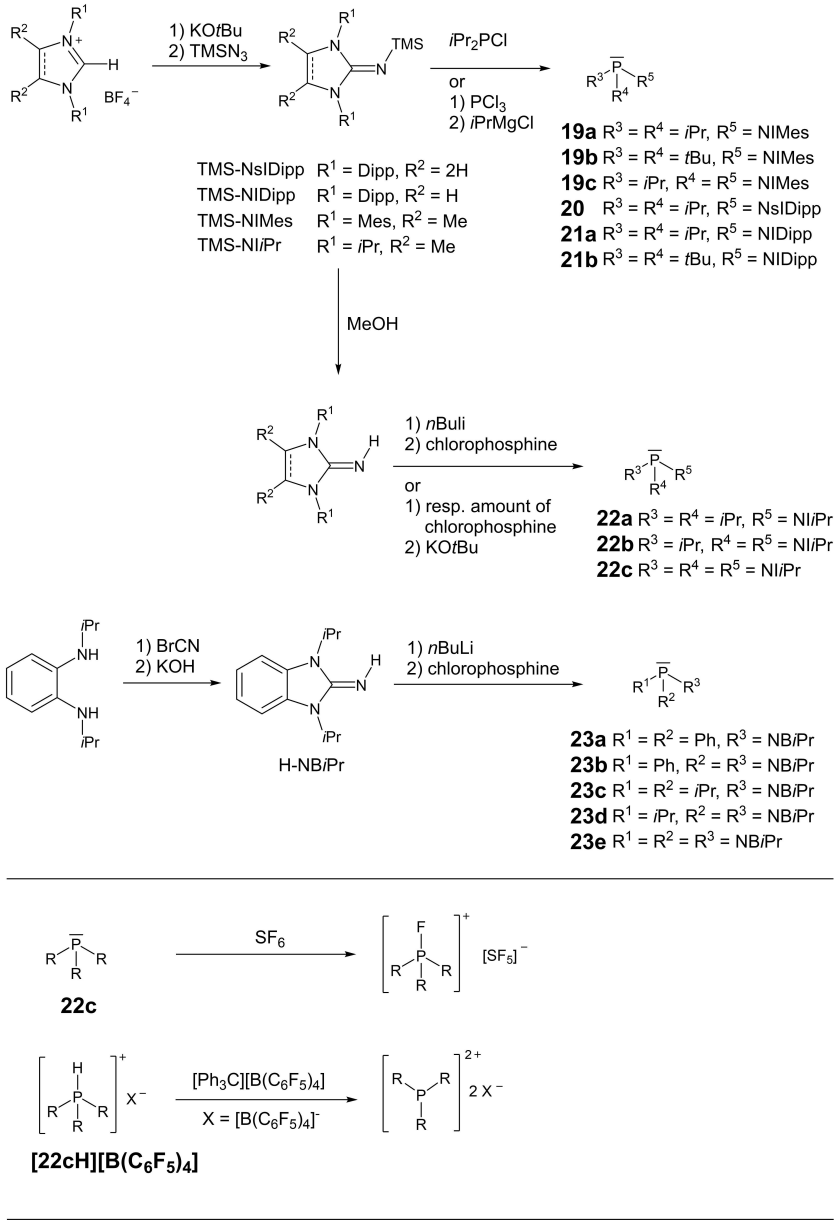
2.1.2. Pyridinylidenamino phosphines (PyAPs)

Taking the results of Nifantyev et al. in consideration,[100] Dielmann and co-workers realized PyAPs (pyridinylidenamino-phosphines) 27–29 by the incorporation of readily available and strongly π-donating pyridinylidenamino substituents in order to manifest cheap and easy-to-prepare electron-rich phosphines for a broad range of applications as ligands or employment in stoichiometric quantities (Scheme 11).[96,101] A comparison of the calculated gas-phase basicities of IAPs and PyAPs based on the representative examples P(NI*i*Pr)$_3$ (22c, 288.0 kcal/mol) and PyAP P(–N=C_5H_4N-*n*Bu)$_3$ (27e, 284.3 kcal/mol) reveal similar proton affinities.[96]

Aminopyridines represent cheap and commercially available starting materials and promise short straightforward PyAP syntheses. Analogous to imidazoline-2-ylidenamino substituents, electronic and steric finetuning of aminopyridines can be easily incorporated with substituents (Scheme 11).

Starting from 2- or 4-aminopyridinium salts the deprotonation with KHMDS and subsequent reaction with R_2PCl delivers the respective mono-PyAPs 27a-d and 28a-d in excellent yields (> 84 %).[101]

As previously reported by Dielmann and co-workers tris-PyAP P(–N=C_5H_4N-*n*Bu)$_3$ (27e, Scheme 11) can be generated in THF solution by treatment of PCl_3 with five equivalents of imine HN=C_5H_4N-*n*Bu and the subsequent deprotonation with KHMDS. However, the clean isolation of 27e is hampered by the incorporation of KCl in the stable coordination adduct 27e·KCl. Due to the increased steric hindrance at the imine nitrogen atom, the respective 2-pyridinylidenamino groups have been



Scheme 9. IAPs of Dielmann et al., their use in SF_6 activation and the synthesis of a phosphorus dication.[9,86–88,94,95]

proven beneficial for the liberation of the corresponding free tris-2-pyridinylidenamino phosphines 29a and 29b from their HBF_4 salts in yields over 81 %.

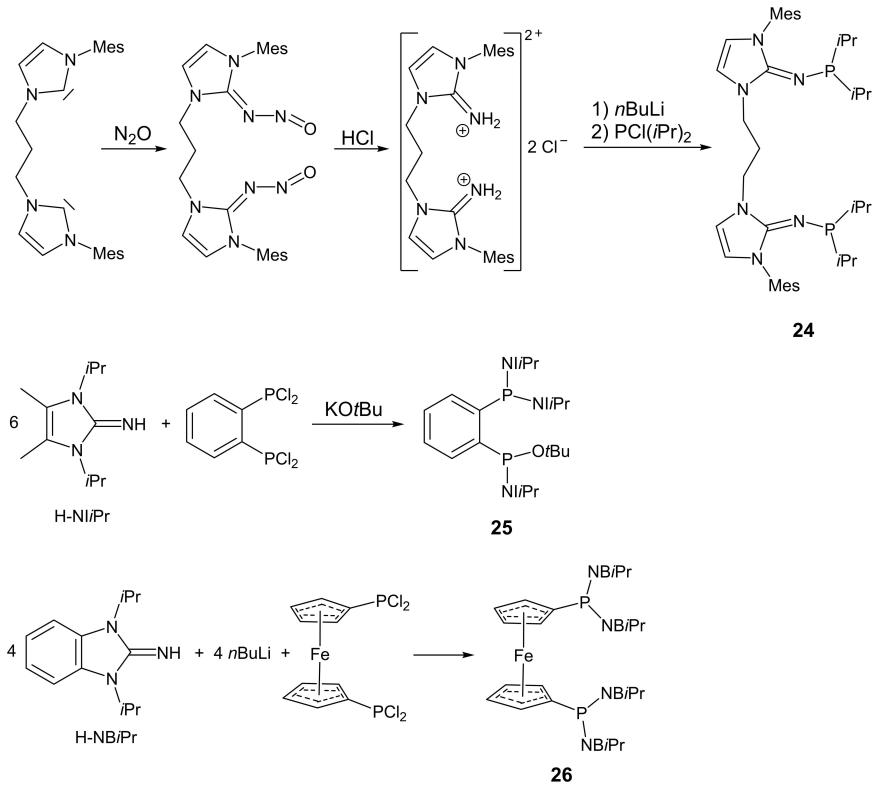
The pronounced Lewis basicity of PyAPs 27–29 is documented by the ready formation of complexes with Cu^I, Au^I and Pd^{II} compounds and moreover is used for the activation of small molecules as SO_2 and CO_2 via incorporation as stable Lewis base adducts.[101] The in situ generation of PyAP 27e and the subsequent disintegration of SF_6 is also reported.[95,96]

2.1.3. Phosphazenyl phosphines (PAPs)

Like all electron-rich phosphines, phosphazenylphosphines (PAPs) represent strong Lewis and Brønsted bases, which is perceptible in their coordination properties.[11,102]

Sundermeyer et al. developed the strongest phosphine Brønsted bases known so far via attachment of Schwesinger's phosphazenyl groups at the tricoordinate P-atom.[103–105]

The monophosphazenylphosphines **30 a–d** are produced by treatment of PCl_3 with the respective phosphanimine $(R_2N)_3P{=}NSiMe_3$ followed by aminolyses (Scheme 12). The applied phosphanimine derivatives are synthesized via a Staudinger reaction with trimethylsilyl azide.[36,104]



Scheme 10. Bidentate IAPs of Dielmann et al.[94]

Phosphazenylphosphines 31a and 31b as well as the biphosphazenyl derivative (dma)P_6P (32) are only accessible in their protonated form starting from $(Me_2N)_2PCl$ or $(Et_2N)_2PCl$, respectively, and reaction with mono- or diphosphazenes in THF solution (Scheme 13).[103–105] Advantageously, the employed dialkylaminochlorophosphines contain a built-in auxiliary base; this avoids the formation of inseparable mixtures of phosphonium and ammonium salts as the products. The subsequent anion exchange reaction with $NaBF_4$ delivers the desired tetrafluoroborate salts in excellent yields (>83%, Scheme 13).

The asymmetrically substituted (dma)P_4P (33) is also obtained as the HBF_4 salt by reaction of PAP 30a with either $[(Me_2N)_3P{=}NH_2][BF_4]$ and $(Me_2N)_3P{=}N{-}P(NMe_2)_2{=}NH$ or $[(Me_2N)_3P{=}N{-}P(NMe_2)_2{=}NH_2]Br$ and $(Me_2N)_3P{=}NH$, respectively, with subsequent salt exchange (Scheme 13).

The free P_3P and P_4P bases **31**a–b and **33** can be liberated from their corresponding phosphonium tetrafluoroborates with potassium hexamethyldisilazide (KHMDS) in toluene solution, yielding the desired products as colorless solids in high yields (>79%, Scheme 13). Unfortunately, the deprotonation of the higher homologue $[(dma)P_6PH][BF_4]$ ([32H][BF_4]) remains a challenge.[103] It could neither be realized with potassium in liquid ammonia or ethylenediamine, nor with several lithium bases (*n*- and *t*BuLi, lithium di-i*so*-propylamide), among others.[103] Solely in the presence of an excessive amount of $NaNH_2$ or potassium pyrrolidide in THF solution could the free base **32** be generated and characterized by NMR spectroscopy.

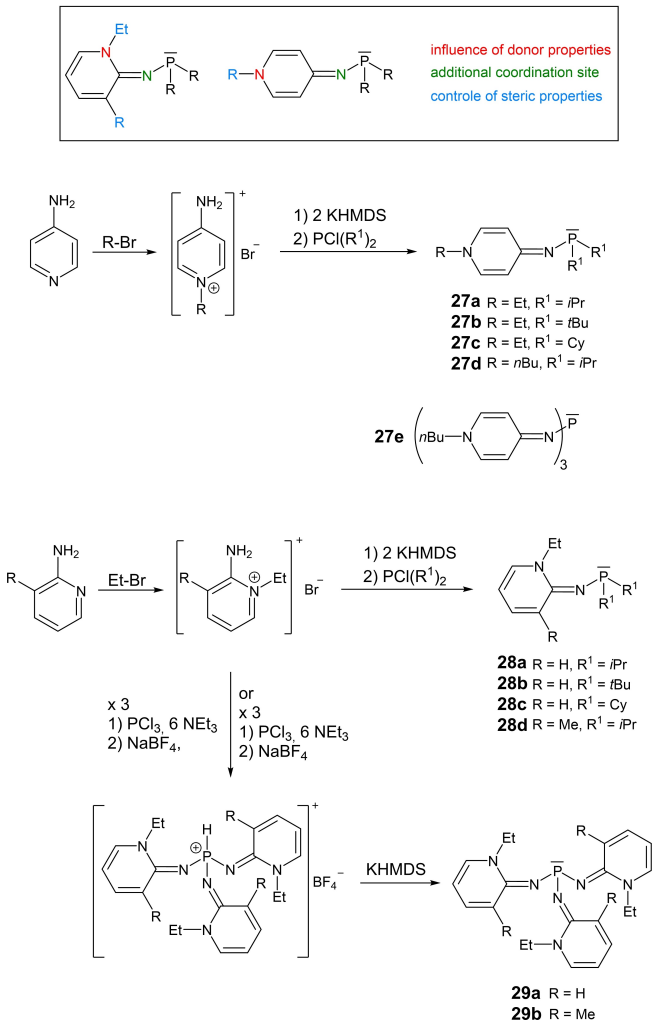
The obtained PAPs exhibit experimental $^{THF}pK_{BH^+}$ values of 34.9 for (dma)P_3P (31a) and 36.7 for (pyrr)P_3P (31b), respectively, and up to 37.2 for (dma)P_4P (33).[103] The $^{THF}pK_{BH^+}$ values of PAPs largely exceed that of the methyl Verkade superbase 14a ($^{THF}pK_{BH^+} = 24.1$) and Dielmanns IAP P(NI*i*Pr)$_3$ (22c, $^{THF}pK_{BH^+} = 31.0$), and may further surpass Schwesinger's methyl tetraphosphazene superbase MeP_4*t*Bu (18a, $^{THF}pK_{BH^+} = 33.9$) and pyrrP_4*t*Bu (18b, $^{THF}pK_{BH^+} = 35.3$).[18,19] The respective mono-PAPs **30**a–d are significantly less basic with calculated $^{MeCN}pK_{BH^+}$ values of 26.4 for methyl derivative 30a up to 31.5 for pyrrolidyl derivative 30d.[104] The corresponding piperidyl- and azepanyl derivatives 30b and 30c show similar $^{MeCN}pK_{BH^+}$ values.

In addition to the remarkably high observed proton affinities of PAPs, they surpass the Lewis basicity of IAPs, PyAPs and YPhos ligands, which is also mirrored in their coordination chemistry.[103] PAP-complexes of gold(I) or platinum(0) are reported to be efficient catalysts for hydroamination reactions of alkynes and hydrosilylations reactions of olefins.[105]

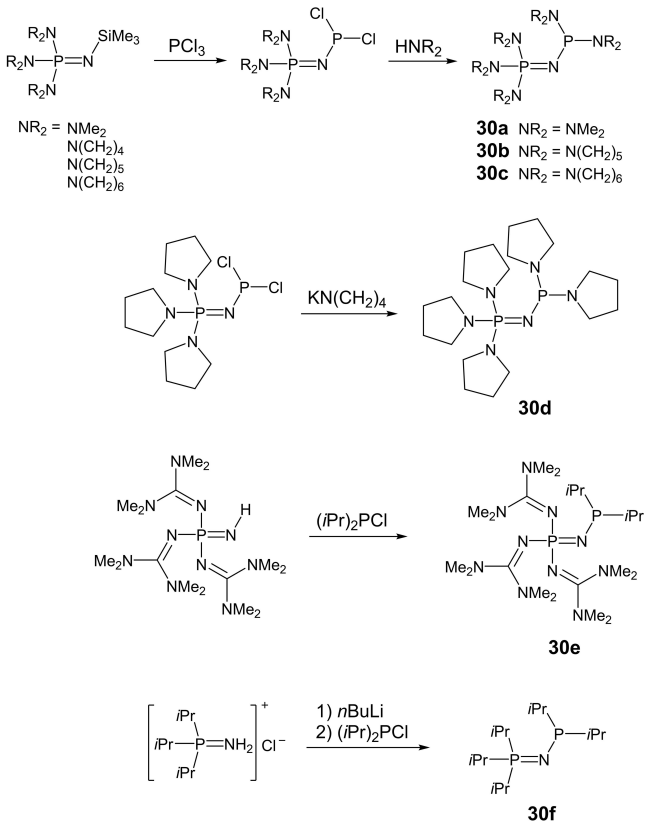
Complementing the row of dialkyl PAPs, Dielmann established the syntheses of phosphazenylphosphines **30e** and **30f**, and gold(I) complexes thereof.[106]

2.1.4. Ylidylphosphines

Phosphonium ylides, bisylides and yldiides are 1,2-dipolar compounds with a high electron density at the central carbon atom.[44–46,107] Thus, they act as strong carbon Brønsted bases



Scheme 11. PyAPs of Dielmann et al. and structure of **27 e**.[96,101]



Scheme 12. Syntheses of mono PAPs.[103,104,106]

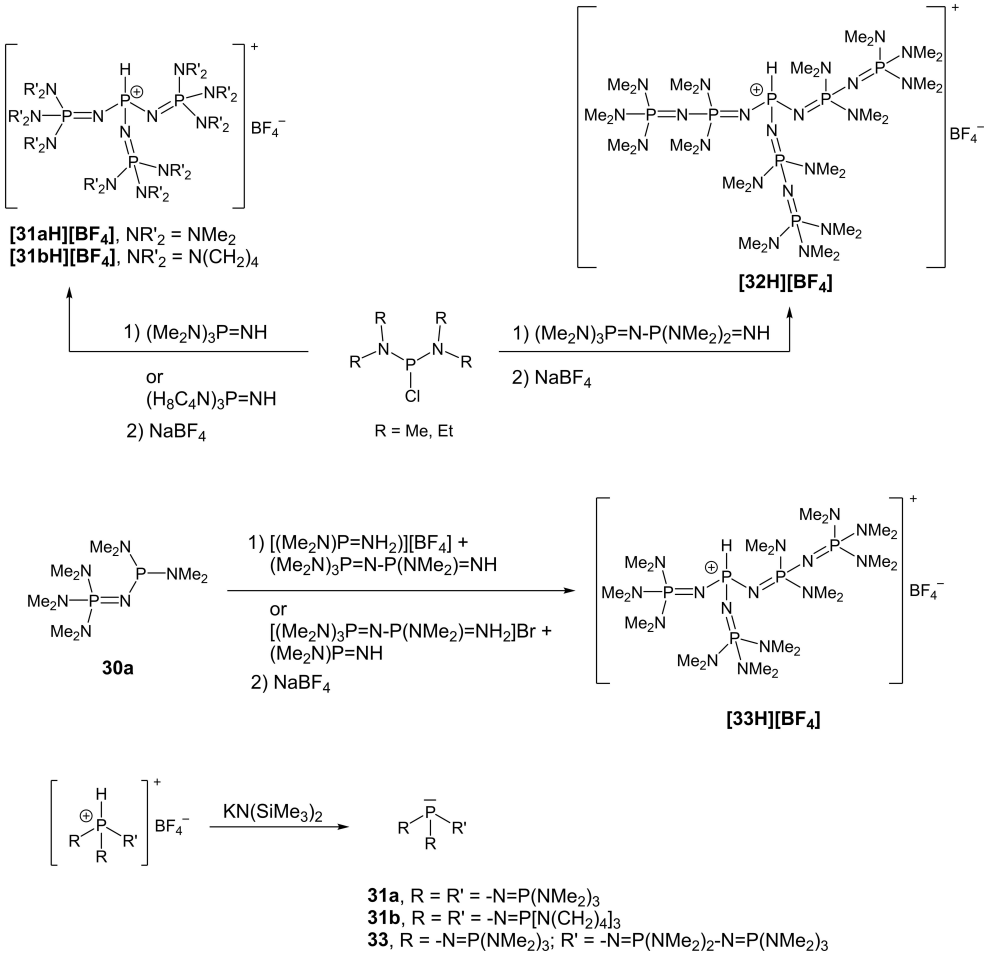
and show a significant tendency for the addition of electrophiles.[19,42] During research on ylide and yldiide compounds as ligands in transition metal complexes and the stabilization of reactive low-valent main group elements, Gessner and co-workers connected the strongly π-donating ylidyl groups as substituents to a phosphorus atom and obtained electron-abundant ylidylphosphines (YPhos).[108,109,110,111,112]

Three simple reaction paths A–C in Scheme 14 were presented to synthesize ylidylphosphines starting from alkylphosphonium salts, which can be easily prepared via reaction of the respective phosphine with alkylhalides (Scheme 14).[113,115] Depending on the nature of Z, double deprotonation with metal bases and subsequent nucleophilic substitution at halophosphines deliver the desired YPhos ligands **34a–e** in moderate to high yields of 69–92% (route A).[115] As demonstrated for 34a, the detour via a reaction of yldiides with PCl_3 (70%) and alkylation with organolithium or Grignard reagents is also feasible, but requires the isolation of sensitive intermediates.[115] In case of cheap starting materials, pathway B is recommendable. Reaction of ylides with halophosphines and deprotonation by a second equivalent of ylide as the auxiliary base afforded the target molecules.[115] Route C is accomplished by treating ylides with halophosphines, but requires an additional equivalent of a base such as KH or KHMDS. Routes B and C are reported to proceed in a one pot synthesis and are therefore the preferable preparation methods.

The corresponding ylidylphosphines Y_HPiPr_2 (34i) and Y_HPPh_2 (34j) were synthesized by Dielmann and co-workers in high yields (>85%) in analogy to the preparation method of Issleib and Lindner[42] by treating ylide H_2CPPh_3 with the respective chlorophosphine (Scheme 14).[106]

The latest findings in palladium catalysis gave rise to rather labile P–C bonds of triphenylphosphonium functionalities in common YPhos ligands, which results in inactive catalytic systems on course of the reaction, Gessner et al. replaced the phenyl by cyclohexyl groups.[108,109,114] The resulting ligands in $^{Cy}Y_{Me}PCy_2$ (**34k–m**) show elevated stability and a remarkable performance in palladium-catalyzed amination reactions of aryl chlorides at room temperature (Scheme 14).[108,109]

YPhos ligands in general represent valuable electron-rich phosphines, which was demonstrated by their readily formation of transition metal complexes, such as gold(I)[106,111,115] or palladium[112–114] complexes, which have been successfully employed as catalysts in amination and hydroamination reactions, as well as alpha arylation with arylchlorides among others.[116]



Scheme 13. Syntheses of tris PAPs.[103–105]

2.2. Phosphazenes

While highly electron-rich phosphines generally find application in transition metal catalyses, low nucleophilic phosphazene Brønsted superbases have been preferably established in deprotonation reactions, which is particularly obvious with regard to the huge variety of commercially available tailor-made phosphazenes as auxiliary bases for nearly every purpose.

2.2.1. Basicity enhancement by hydrogen bonding

While several useful methods are known to increase the Brønsted basicity of phosphazene bases, the group of Sundermeyer studied the stabilizing effect of hydrogen bonding in detail and thereby designed the first phosphazene superbase TDMPP (**35**) with an increased basicity due to multiple intramolecular hydrogen bonding (Scheme 15).[117]

Phosphazene **35** is obtained as its corresponding phosphazenium tetrafluoroborate by the reaction of 3-dimethylamino-1-propylamine with PCl_5 and subsequent salt metathesis reaction in 68% yield. The following deprotonation with KO*t*Bu proceeds nearly quantitatively (98%).

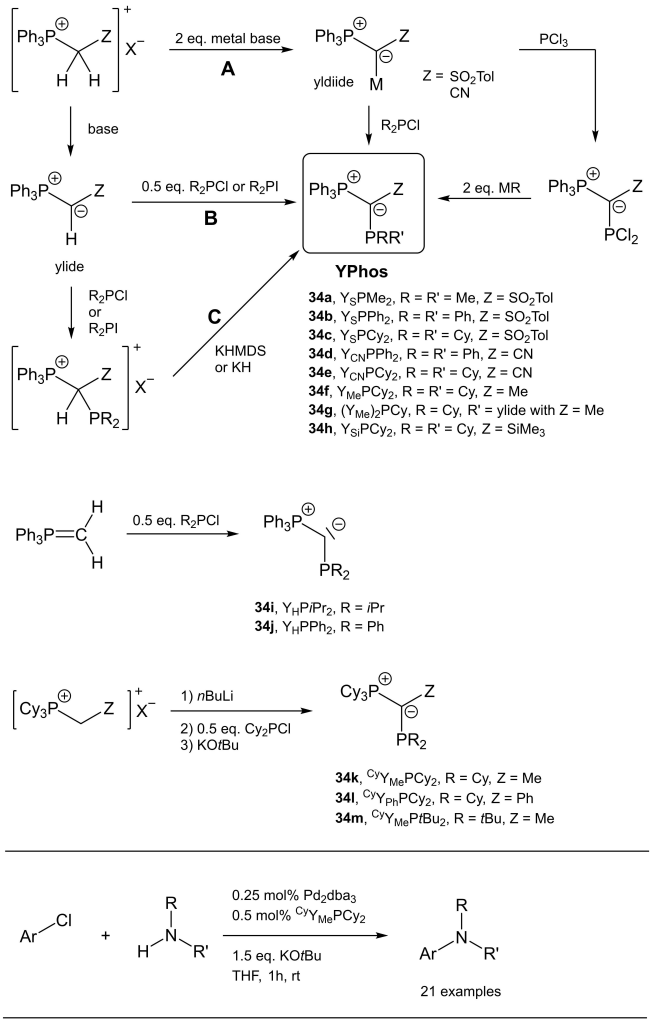
X-ray crystallographic analyses revealed shorter and thus stronger hydrogen bonds within the protonated base **35**H]$^+$ with N–(H)···N distances of 296 pm, compared to free **35** with distances of 300 to 305 pm.[117]

Due to multiple intramolecular hydrogen bonding, **35** exhibits a basicity of $^{MeCN}pK_{BH^+} = 30.4$, which is enhanced by up to 2.9 and 1.5 orders of magnitude relative to the presently known monophosphazenes $(Me_2N)_3P{=}NMe$ and $[(H_2C)_4N]_3P{=}NEt$.[18,117]

2.2.2. Proton sponges derived from phosphazenes

The combination of Alders proton sponge 1,8-bis(dimethylamino)naphthalene (DMAN)[4,118] with superbasic phosphazenyl fragments constitutes the class of phosphazene proton sponges (Scheme 16).[119–123]

Sundermeyer's prototypical HMPN (1,8-bis(hexamethyltriaminophosphazenyl)naphthalene, **36a**), published in 2005, is accessible via a Kirsanov reaction with subsequent deprotonation (43%, Scheme 16).[119–121,123] HMPN (**36a**) has a proton affinity of PA = 274 kcal/mol and a $^{MeCN}pK_{BH^+}$ value of 29.9, and is thus 12 orders of magnitude more basic



Scheme 14. Syntheses of YPhos ligands and an example of their use in palladium-catalyzed amination of aryl chlorides.[108,113–115]

than DMAN and four orders more basic than TMGN (1,8-bis(tetramethylguanidyl)naphthalene).[119,124] As the success of Kirsanov type reactions is limited for sterically demanding groups, the pyrrolidine-derivative TPPN (**36b**) and its higher homologue P_2-TPPN (**37a**) are only viable from Staudinger reactions starting from 1,8-bis(diazido)naphthalene. The proton pincer ligands **36b** and **37a** reach extremely high $^{MeCN}pK_{BH^+}$ values of 32.3 and 42.1, respectively,[120,121] whereas a significant nucleophilicity of phosphazenyl proton sponges was observed in the reaction with ethyl iodide. While in case of **37a** complete protonation in a dehydrohalogenation reaction is observed, for the less bulky proton sponges **36a** and **36b** alkylation is favored over elimination reactions. This is also the case for alkyl substituted biphosphazenyl proton sponges.[123] The corresponding monosubstituted naphthalene derivatives were shown to be significantly less basic; this is due to the loss of stabilizing intramolecular hydrogen bonding in the protonated form.[119,120]

Interestingly, Sundermeyer et al. observed a significant stability of biphosphazides as intermediates in the Staudinger reactions and obtained the respective compounds in moderate to high yields (Scheme 16).[104,121] By definite reaction conditions monophosphazide **36b**(1 N_2) could also be prepared (Scheme 16).

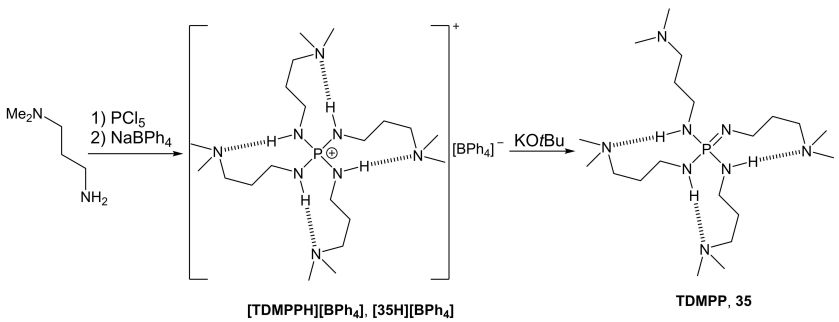
Except for the compounds **36a**(2 N_2), **36b**(2 N_2) and **37a** (2 N_2), which feature relatively small NR_2 groups and thus are prone to thermally induced nitrogen extrusion to yield the phosphazenes **36a**–**b** and **37a**, all other biphosphazides are highly stable even at elevated temperatures, for which the bulky substituents were made responsible.[121]

Due to their high nucleophilicity, the proton sponges do not only act as proton acceptors, but also readily form pincer complexes with Lewis acids, such as $AlMe_3$ and $GaMe_3$.[123]

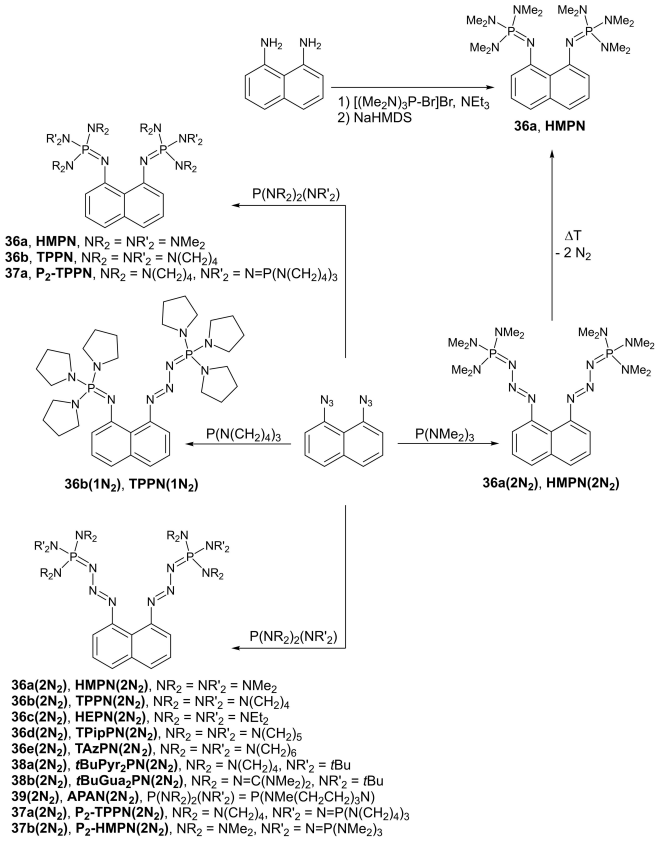
2.2.3. Chiral phosphazenes

The employment of chiral organocatalysts bearing strongly Brønsted basic phosphazene moieties for the activation of only weakly acidic pronucleophiles has been introduced for the first time in the asymmetric Henry reaction by Ooi et al. in 2007.[125,126]

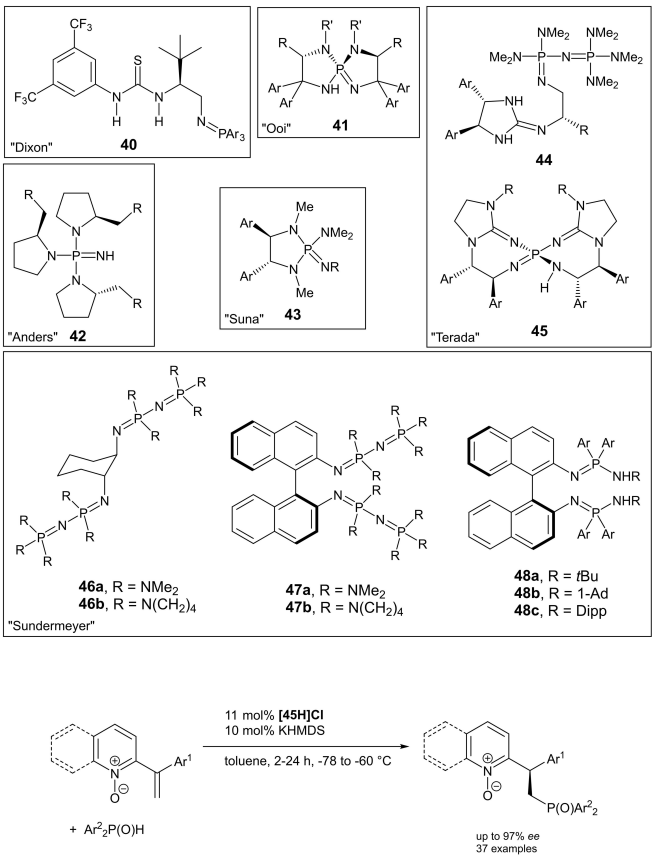
The good availability of chiral phosphazenes[127] and their outstanding catalytic activity in enantioselective sulfa-Michael addition reactions,[128] Mannich-type reactions,[129] cycloaddition reactions,[130] hydrophosphinylations[131] as well as 1,2- and 1–4-addition reactions[132] among others has moved them into the focus of current interest. Rigid chiral iminophosphoranes are excellent reagents for challenging enantioselective reactions as



Scheme 15. Synthesis of TDMPP (**35**).



Scheme 16. Phosphazenyl and phosphazide proton sponges.



Scheme 17. Chiral phosphazene bases and enantioselective hydrophosphinylation reaction.[131]

well.[133] The hydrophosphinylation reaction with Terada's phosphazene depicted in Scheme 17 provides insight into the broad spectrum of possible substrates and the formation of valuable products with high enantioselectivities (up to 97 % *ee*).

The chiral iminophosphoranes **40** of Dixon,[128,132,134,135] spirophosphazenes **41** of Ooi[125,136] and chiral guanidinophosphazenes **44** and **45** of Terada[129–131,137,138,139] are depicted in Scheme 17, but will not be discussed in more detail, since latest advances and achievements have been reviewed recently.[126,140] The chiral phosphazenes **43** and **42** of Suna[141] and Anders[142] are also included (Scheme 17).

The basicity of chiral phosphazenes can be increased by the homologization strategy of Schwesinger,[16] which was realized by Terada with the cooperative binary base catalyst **44** consisting of a biphosphazenyl unit bound to a guanidyl substituent (Scheme 17), and which has proven beneficial for enantioselective direct Mannich-type reactions.[138]

Sundermeyer et al. focused on two biphosphazene units connected via binaphthyl[122] or cyclohexyl[143] backbones in **47 a**,**b** and **46 a**,**b**. Whereas biphosphazenes **47 a**,**b** can be regarded as proton sponge derivatives, the cyclohexyl derivatives **46 a**,**b** cannot be considered as such due to the lack of N-electron pair repulsion.[143]

Chiral phosphazene bases are accessible by prominent methods such as Staudinger reactions of phosphines with chiral azide compounds,[134] by Kirsanov-type reactions,[122,143] by condensation of chiral amines,[142] diamines[125] or guanidines[137] with PCl_5, and combinations thereof.[141]

2.2.4. Carbon superbases containing phosphazenyl groups

As already mentioned, phosphorus ylides behave like phosphonium-substituted carbanions,[44–46] and are thus significantly more Brønsted basic than their corresponding phosphanimine analogues.[19,42] Recent achievements in carbodiphosphorane chemistry have been summarized by Alcarazo[52] and will not be discussed in more detail here. However, it should be briefly noted, that Gessner et al. recently explored a Lewis basic diamino-substituted carbodiphosphorane with strong C-donor properties, that preferentially binds to neutral metals and main group elements via the carbon center instead of the amino groups.[144]

In order to design a Brønsted carbon superbase that overcomes the basicity of Schwesinger's commercially available tetraphosphazenes **18** and additionally features a significantly decreased molecular weight, Sundermeyer and co-workers focused on the classical proton sponge concept and brought the basicity centers of phosphonium ylides in spatial proximity.[145]

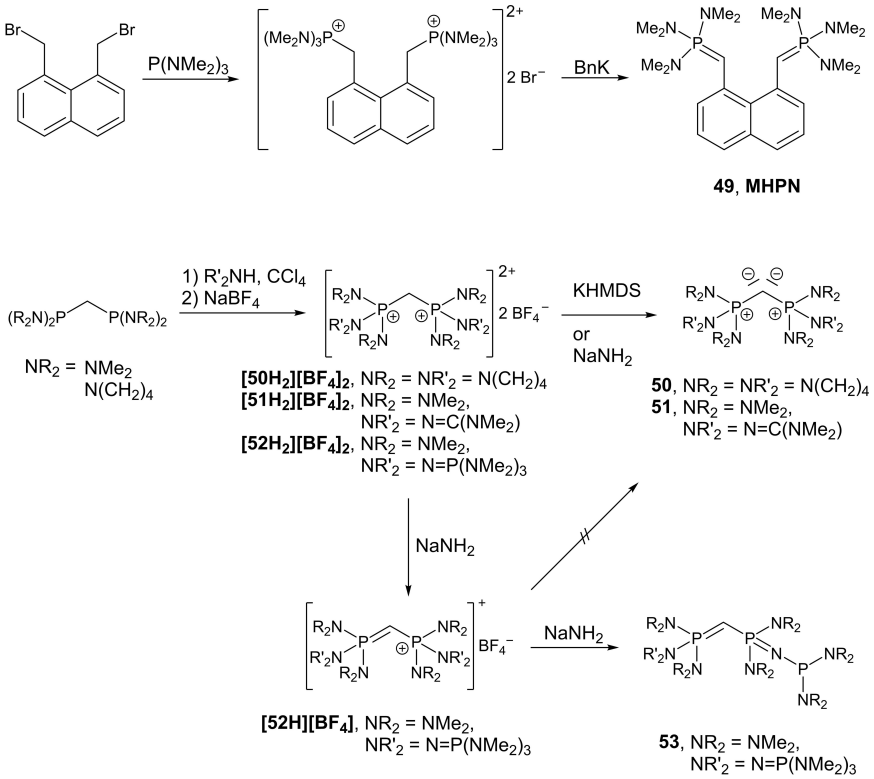
The nucleophilic substitution of 1,8-bis(bromomethyl) naphthalene with $P(NMe_2)_3$ and the subsequent deprotonation with benzyl potassium afforded the desired carbon-based proton sponge MHPN (**49**) in a 84% yield (Scheme 18). NMR spectroscopic titration experiments revealed a significantly enhanced basicity of **49** ($^{MeCN}pK_{BH^+} = 33.3$) relative to the biphosphazenyl proton sponge HMPN (**36a**, $^{MeCN}pK_{BH^+} = 29.9$),[145] although no rigid hydrogen bond interaction is found in [**49**H]$^+$. The "acidic" proton bound at carbon undergoes a rather rapid exchange or "proton hopping" between both basicity centers, which is accompanied by an increased kinetic barrier relative to classical proton sponges. Thus, definite CH and CH_2 resonances can be observed by ^{1}H NMR spectroscopy and X-ray diffraction confirms predicted different structures of $CP(NMe_2)_3$ groups in [**49**H]$^+$.

As no beneficial basicity increase by interaction of two carbon basicity centers in spatial proximity was proven, the direct comparison of ylide **49** with ylide $Me_2C{=}P(NMe_2)_3$ ($^{MeCN}pK_{BH^+} = 37.7$)[19] suggests a possibly larger increase by implementation of strongly electron-donating substituents at the carbon basicity center. For this purpose, Sundermeyer et al. developed a series of carbodiphosphorane derivatives **50**–**52** containing $-P(NR_2)_2(NR'_2)$ groups at the carbon atom, whereas NR'_2 represents already established phosphazenyl, tetramethylguanidyl (TMG) or simple amino groups.[146] Starting from readily available bis(dimethylaminophosphino)methane or the respective pyrrolidyl derivative, oxidative amination with CCl_4 afforded the desired dicationic species in all cases (Scheme 18), which were transferred into their air and water stable HBF_4 salts according to described literature procedures. The neutral carbodiphosphoranes **50** ($^{THF}pK_{BH^+} = 30.1$–32.9) and **51** ($^{THF}pK_{BH^+} = 35.8$) were liberated via twofold deprotonation with KHMDS or $NaNH_2$ in yields of 60% and 70%, respectively.[146] Guanidyl derivative **51** is the strongest carbon Brønsted base presently known and surpasses ylide $H_2C{=}P(2,4,6\text{-}(MeO)_3\text{-}C_6H_2)_2Ph$ with a $^{THF}pK_{BH^+}$ value of 33.5.[19]

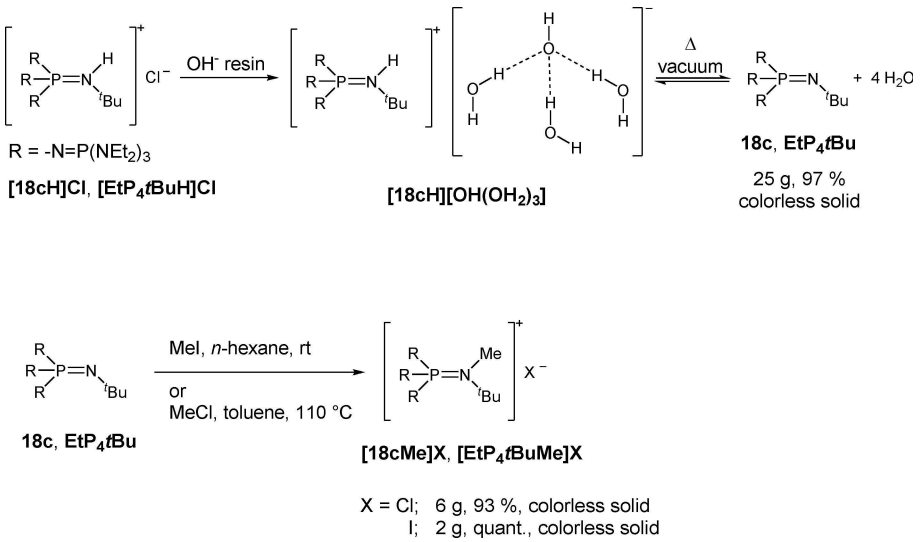
The higher dicationic phosphazenyl homologue $[\mathbf{52}H_2]^{2+}$ can be efficiently transferred into the monocation [**52**H]$^+$ by treatment with $NaNH_2$ (69%, Scheme 18). A second deprotonation step at the carbon atom, however, does not occur. In contrast to the desired carbodiphosphorane **52** (calculated $^{THF}pK_{BH^+} = 39.1$), Sundermeyer obtained the phosphazenylphosphine **53** as the selective product via elimination of a peripheric dimethylamino group, by which he clearly demonstrated a potential basicity limit for dimethylaminophosphazene-incorporated superbases.[146]

2.2.5. Non-coordinated anions with phosphazene bases

Most commonly, phosphazene bases are required for the deprotonation of only weakly acidic pronucleophiles, as the trifluoromethane building block in nucleophilic trifluoromethylations.[147,148] Moreover, the low Lewis acidity of the corresponding phosphazenium cation makes the formation of non-coordinated "naked" anions possible, which feature a drastically increased reactivity. Combinations of phosphazene Brønsted bases with protic reactants are thus frequently used as metal-



Scheme 18. Syntheses of carbodiphosphoranes.



Scheme 19. Liberation of tetraphosphazene **18c** via its hydroxide hydrate salt and ensuing methylation.[157,159]

free promotors in anionic polymerizations[149] such as of γ-butyrolactone,[150] methyl methacrylate,[151] cyclosiloxanes[152] or in copolymerizations of epoxides.[153]

Clearly, the nature of the respective non-coordinated anionic species is of broad interest for the elucidation of structural features and the stability of intermediates, as well as an insight into conceivable reaction pathways, as prerequisites for an improved fabrication of products and reliable quantum chemical predictions.

Recently, we were able to trap a row of such saline phosphazenium salts formed by the deprotonation of protic additives and elucidated their structures. This allows significant insights into the nature of formed "naked" anions and the partially necessity of stabilization via hydrogen bonding, as presented in more detail for silanol-silanolate anions,[154,155] non-coordinated phenolate anions and their phenol-phenolate adducts.[156]

The hydroxide trihydrate anion, $[OH(OH_2)_3]^-$, obtained by the reaction of water with the perethyl tetraphosphazene base $[(Et_2N)_3P{=}N]_3P{=}NtBu$ (**18c**, Scheme 19), represents the first hydroxide hydrate devoid of significant cation-anion interactions (Figure 2, top) and thus, contains three water molecules bonded via hydrogen bridges.[147]

In a similar manner, the deprotonation of *tert*-butanol delivers a *tert*-butanolate anion with two *tert*-butanol solvate molecules, confirmed by X-ray analysis of single crystals of [**18c**H][*t*BuO(HO*t*Bu)$_2$][157] obtained from a cooled *n*-hexane reaction mixture (Figure 2, bottom right).[158]

The O1–O2 and O1–O3 distances in the anion amount to 258.2(2) and 253.0(2) pm, respectively, and are similar to those observed in the trimethylsilanolate anion $[Me_3SiO(HOSiMe_3)_2]^-$ previously reported by us (Figure 2, bottom left).[154] Solid [**18c**H][*t*BuO(HO*t*Bu)$_2$] decomposes readily upon warming to room temperature and partially reformation of the free base **18c** is evident by ^{31}P NMR spectroscopy.

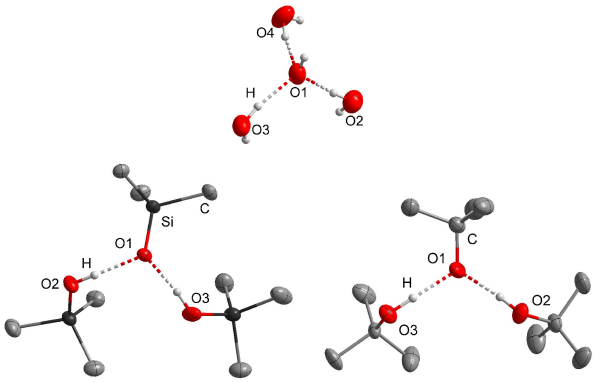


Figure 2. Anions of the phosphazenium salts [**18c**H][OH(OH$_2$)$_3$] (top),[147] [**18c**H][Me$_3$SiO(HOSiMe$_3$)$_2$] (bottom left)[154] and [**18c**H][*t*BuO(HO*t*Bu)$_2$] (bottom right).[158] The cation [**18c**H]$^+$ is not depicted.

In general, solvated anions $[OH(OH_2)_3]^-$, $[tBuO(HOtBu)_2]^-$ and $[Me_3SiO(HOSiMe_3)_2]^-$ are prone to loss of the solvate shell, with concomitant deprotonation of their phosphazenium cations [**18c**H]$^+$.[147,154] The equilibrium reaction was investigated in more detail by ^{31}P NMR spectroscopic titration of **18c** with water[147] and *tert*-butanol.[158] In general, mixtures consisting of free and protonated phosphazene base **18c** and [**18c**H]$^+$ contain two separated signal sets with characteristic $^2J_{PP}$ couplings of 29 Hz and 70 Hz due to a high kinetic proton exchange barrier at ambient temperature, as obvious in ^{31}P NMR spectra of the titration of **18c** with *tert*-butanol (Figure 3).

In contrast, a significantly accelerated proton exchange between [**18c**H]$^+$ and hydroxide anions seems present (Figure 4). With increasing amounts of water just one single signal set is observed with a continuous increasing $^2J_{PP}$ coupling constant from 29 to 70 Hz.[147] This laid the foundation stone for the preparation of **18c** in a high-yield deprotonation step (> 97%) via salt exchange of [**18c**]Cl with a basic anion exchange resin and the subsequent thermolysis of the formed hydroxide

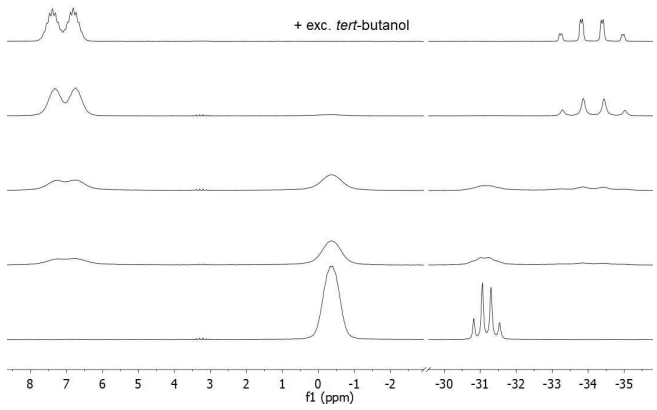


Figure 3. ^{31}P NMR spectroscopic titration of **18c** with *tert*-butanol in chlorobenzene. Lock with [D$_6$]acetone in a capillary. Bottom: free base; top: with an excess of *tert*-butanol.[158]

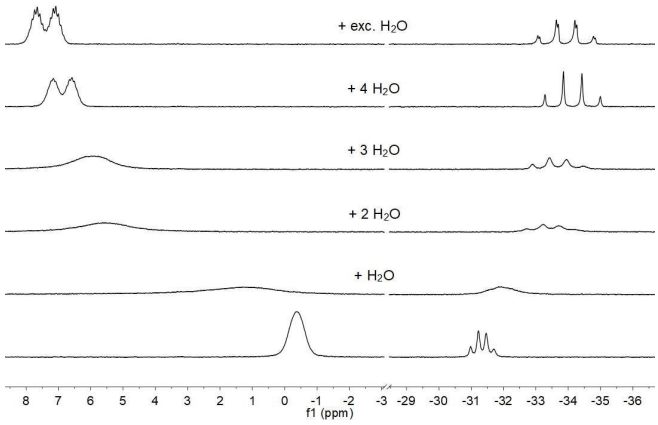


Figure 4. ^{31}P NMR spectroscopic titration of **18c** with different amounts of water in chlorobenzene. Lock with [D$_6$]acetone in a capillary. Bottom: free base; top: with an excess of water.[147]

salt (Scheme 19).[147] This circumvents the common way[16,62] employing hazardous and self-igniting amide salts in liquid ammonia.

We clearly demonstrated that the "acidic" iminium functionality of [**18c**H]$^+$ needs protection for trapping a "naked" hydroxide anion. The substitution of the proton by a methyl group in [**18c**Me]$^+$ seems promising and can be incorporated by alkylation of base **18c** with methyl halides (Scheme 19).[62] Whereas methylation of **18c** is performed quantitatively with MeI in *n*-hexane at ambient temperature, the analogous reaction with MeCl solely afforded the protonated base under the same conditions, however, methylation is favored over protonation in toluene at elevated temperatures.[158]

The methylated base [**18c**Me]$^+$ features a characteristic quartet of quartet splitting with $^2J_{PP}$ and $^3J_{PH}$ couplings of 77 and 14 Hz. For the generation of a phosphazenium hydroxide salt the described procedure by means of a basic anion exchange resin was applied.[147] Subsequent drying in a high vacuum at ambient temperature already resulted in the deterioration of the phosphazenium cation [**18c**Me]$^+$ and led to a mixture of products. Multinuclear NMR spectroscopy suggests the decomposition of the *tert*-butyl group of the iminium functionality as the main decomposition pathway. Thus, the generation of a naked hydroxide anion in the presence of peralkylated phosphazenium cation [**18c**Me]$^+$ seems to exceed the limits of the respective protocol.

3. Conclusions and Outlook

In this minireview, we have given an account of the most recent developments in the chemistry of electron-rich phosphines and phosphazenes. Strategies to increase the Lewis and Brønsted basicity of electron-rich phosphines are based upon the introduction of strongly π-donating substituents. The phosphazenyl groups introduced by Schwesinger are particularly suitable for this purpose, as they exert a considerable influence on the electronic structure of the central atom through the homologization strategy. The corresponding phosphazenyl phosphines (PAPs) can even surpass the basicity of Schwesinger's commercially available tetraphosphazene bases. Furthermore, incorporation of NHC-based imidazolin-2-ylideneamino groups have also proven beneficial. The known NHC backbones allow efficient fine-tuning of the electronic and steric properties of the corresponding imidazolin-2-ylideneaminophosphines (IAPs). Similar donating abilities have also been demonstrated for pyridinyliden-2-amino groups in pyridinyliden-2-amino phosphines (PyAPs), which are extremely cheap alternatives to IAPs. Ylidyl groups in ylidylphosphines (YPhos) are also suitable for enhancing the Lewis basicity and to generate efficient transition metal catalysts.

As Schwesinger's homologization concept for increasing the Brønsted basicity of phosphazenes has already reached its limits, there are versatile approaches to increase the basicity by steric effects. For example, it has been shown that the basicity of phosphazenes is significantly increased by the formation of intramolecular hydrogen bonds in their protonated form. It is also possible to combine the structure of proton sponges with electron-donating phosphazenyl groups, thus exceeding the basicity of the conventional proton sponge 1,8-bis (dimethylamino)naphthalene by several orders of magnitude. The inclusion of chiral substituents at the phosphorus atom or the attachment of phosphazene units to chiral backbones has enabled the preparation of a variety of chiral phosphazenes, allowing the catalytic and stereoselective conversion of weakly acidic pronucleophiles.

In contrast to superbasic phosphines, which tend to add electrophiles and are therefore used for transition-metal-catalyzed coupling reactions, sterically encumbered tetraphosphazene bases offer the possibility to deprotonate weakly acidic compounds and, due to their low tendency for coordination, allow the study of the corresponding non-coordinated anions.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: electron-rich · naked anions · phosphazene · phosphine · superbases

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