Intrinsic Basicities of Phosphorus Imines and Ylides: A Theoretical Study

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A density functional theory (B3LYP/6-311+G**), ab initio (HF/3-21G*), and semiempirical (PM3) study of intrinsic basicities, protonation energies, or protonation enthalpies of organic phosphorus imine (iminophosphorane) including phosphazene, phosphorus ylide (phosphorane), and phosphine superbases has been performed. The study shows that representatives of the first two classes of the above-mentioned organic superbases can reach the basicity level of the strongest inorganic superbases such as alkali-metal hydroxides, hydrides, and oxides. The strongest organic phosphazene imine superbases are predicted to reach the gas-phase basicity level of ca. 300 kcal/mol (number of phosphorus atoms in the system $n \geq 7$), whereas the strongest organic phosphazene ylide superbases are estimated to have (at $n \geq 5$) gas-phase basicities around or beyond 310−320 kcal/mol. The phosphine superbases, including the Verkade's bicyclic phosphines (proazaphosphatranes) are predicted to have a basicity comparable to P_2 phosphazenes or P_1 phosphorus ylides, whereas the respective proazaphosphatrane imines and ylides are expected to be the strongest organic superbases which contain only a single phosphorus atom. Extremely high expected basicity values and handling preferences over inorganic superbases make representatives of novel organic superbases possible partners for observing the spontaneous gas-phase proton transfer between neutral Brønsted superacids and -bases. For the comparison, the basicities of some alkali-metal substituted ammonia, phosphine, phosphorus, and nitrogen ylides and imines have been also calculated.

Introduction

The alkali-metal (M) hydroxides MOH and oxides M_2O are neutral Brønsted bases with the highest experimentally measured intrinsic basicities/proton affinities found so far.[1−3] The gas-phase basicity values of alkali-metal hydroxides range from 240 kcal/mol (LiOH) to 272 kcal/mol (CsOH), whereas the same quantities for the corresponding alkali-metal oxides cover the interval from 281 (Li_2O) to 337 kcal/mol (Cs_2O). This means that the intrinsic basicity of strong neutral bases exceeds, in these cases, the basicity of the weakest anionic bases which form by deprotonation of strong neutral Brønsted acids. Alkali-metal hydroxides and oxides form an important family of superbases with wide area of applications. However, low solubility in most organic solvents, sensitivity to moisture and CO_2 (especially in the case of alkali-metal oxides), low selectivity, and difficulties of handling limit their use in synthetic chemistry, where a wide range of organic superbases, although less basic, is used.

The established gas-phase basicity scale of the strongest neutral organic superbases (guanidine and its acyclic (tetramethylguanidine) or bicyclic (substituted 1,5,7-triazabicyclo[4.4.0]-dec-5-enes) derivatives, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), various proton sponges, etc.) extends to 245 kcal/mol.[1,4−6] Attempts to measure even evidently stronger organic bases, e.g., different representatives of the family of phosphorus imines (phosphazenes, e.g., MeP_1, t-BuP_1, EtP_2, t-BuP_2, t-BuP_4, BEMP, etc.; see Scheme 1)[7−9] and some other types of bases, e.g., diaminovinamidines,[9b] have so far been extremely complicated,[4,5] either because of the lack of convenient reference bases or because of other problems (extensive fragmentation upon electron impact, presence of moisture, CO_2, etc.).

At the same time, pK_a measurements in acetonitrile or DMSO solution show that phosphazenes surpass in their basicity the derivatives of acyclic or bicyclic guanidines, amidines, and diaminovinamidines.[8,9] So, the most widely used phosphazene superbase t-BuP_4 (pK_a(DMSO) = 30.3; pK_a(MeCN) = 42.7) exceeds by a very wide margin[8,9] the respective pK_a values of guanidine (pK_a(DMSO) = 13.9)[10] or DBU[9] (pK_a(MeCN) = 24.1).[11]

Ylides of P, N, and S form another widely studied[7,12] family of potentially superstrong neutral organic bases. The solution data indicate[13] that the $Ph_3P{=}CH_2$ ylide is in DMSO (pK_a = 22.5) 12 powers of 10 more basic than ammonia or roughly of the same basicity as t-$OctP_2$ but by 6 pK_a units stronger base than BEMP (MeCN).[9] However, the pK_a values of presumably much stronger bases such as $Me_3P{=}CH_2$ and $Me_3N{=}CH_2$ are not yet available. We are not aware of any successful attempts to measure the intrinsic basicity of any ylides in the gas phase. A promising approach for designing superstrong neutral organic bases whose intrinsic basicity is expected to exceed 300 kcal/mol was recently suggested on the basis of derivatives of quinodiimines and semiquinodiimines by Maksic

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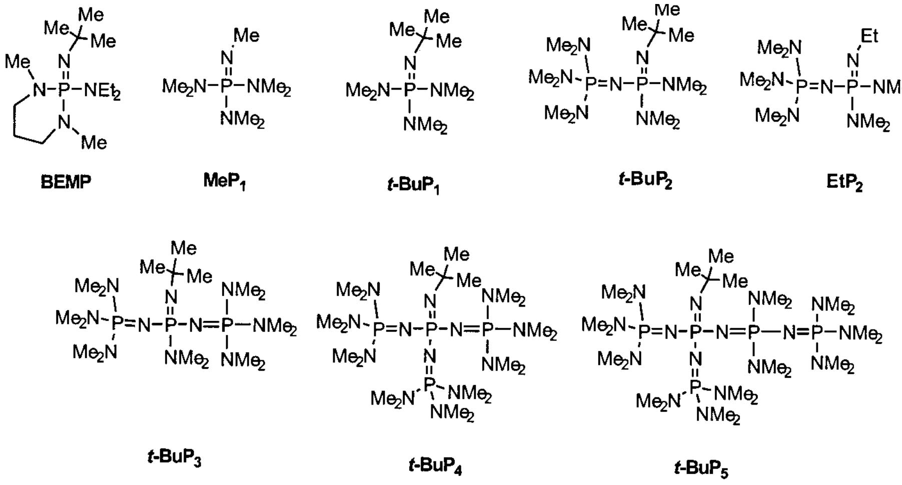
SCHEME 1



and Kovacevic.[14] Similar basicity was recently predicted[15] for Li and Na substituted ammonia.

On the basis of different solution-phase data, Verkade et al. have suggested[16] that their bicyclooctane phosphine (proazaphosphatrane) superbases almost reach the basicity of the widely used t-BuP$_4$ phosphazene superbase. However, in a very recent publication,[17] the basicity of P(MeNCH$_2$CH$_2$)$_3$N and its analogues was reevaluated and drastically (by ca. 8 powers of 10) downgraded to the region of EtP$_2$ bases (pK_a around 33 in MeCN solution).

In the present work, we followed two major goals. The first was to make a reasonable solid estimate of the absolute values of the intrinsic basicities of the simplest representatives of the phosphorus imine and ylide families using model calculations with density functional theory at the B3LYP/6-311+G** level. For comparison, the basicities of representatives of some other classes of compounds (e.g., guanidine, different phosphine derivatives, ylides of elements (N, O, S, C, and Si) other than P, etc.) were also calculated at the same level of theory.

Another aim of this work was, using ab initio and semiempirical calculations at lower level of theory, to study the general trends of changing of the basicity (protonation energy) of phosphorus ylides and imines by variyng their structures (the number of phosphorus atoms, the nature of substituents, the type of branching of the skeleton of the moiety and the position of the basic center, the nature of the bridge between P atoms, etc.) and electronic structure in order to pursue the goal of designing and synthesizing novel and possibly even stronger superbases.

Experimental Section

Computational Details. The computations reported in this work were carried out using the Gaussian 98 series of programs[18] on IRIX-based SGI Origin 200 workstations. Also, the Spartan 5.0 system was used for some ab initio and semiempirical calculations. Density functional theory (DFT) calculations were performed for relatively simple representatives of phosphorus imine and ylide families. B3LYP hybrid functional which includes Becke's exchange functional and the correlation part due to Lee, Yang, and Parr (LYP) were used. Full geometry optimizations and vibrational analyses were performed using the 6-311+G** basis set. This approach has been recently demonstrated[19] by some of us to describe with reasonable accuracy the gas-phase basicities and acidities of a wide variety of relatively simple bases and acids. All stationary points were found to be true minima (NImag = 0). Unscaled B3LYP/6-311+G** frequencies were used to calculate the gas-phase basicities (GB) and proton affinities (PA) of neutral bases (B) taking into account zero-point energies, finite temperature (0−298 K) correction, the pressure−volume work term, and entropy term as appropriate:

$$\mathrm{B} + \mathrm{H}^+ \underset{\Delta H_1}{\overset{\Delta G_1}{\rightleftharpoons}} \mathrm{BH}^+$$
$$\mathrm{GB} = -\Delta G_1$$
$$\mathrm{PA} = -\Delta H_1 \qquad (1)$$

The results of these calculations are listed in Tables 1−5. Some optimized structures of neutral molecules and their protonated forms are given in the Supporting Information (Figure 1S). The optimized geometries of all species are available from the authors upon request. DFT B3LYP/6-31+G* calculations were used to get a reasonable estimate of the absolute GB and PA values for (H$_2$N)$_3$P=NP(NH$_2$)(=NH)N=P(NH$_2$)$_3$ and (H$_2$N)$_3$-P=N−P(NH$_2$)(=CH$_2$)−N=P(NH$_2$)$_3$.

DFT B3LYP/6-31+G* calculations get rather time-consuming in case of simple (H or NH$_2$ at P atoms) phosphorus ylides and imines that include more than three P atoms adjacent to the basicity center. In the case of polyalkylated derivatives including dimethylamino groups at P atoms, the calculations did not include species with more than one P atom. Even in this case the CPU (R10000) time for compounds such as (Me$_2$N)$_3$P=NH and (Me$_2$N)$_3$P=CH$_2$ was ca. 1 month. Therefore, ab initio and semiempirical calculations, at a lower level of theory than in previous section, were used in order to get a general overview of the changes of the protonation energies of phosphorus ylide and phosphazene series with the structure. To save CPU time, high-level calculations of hypothetical compounds with hydrogen on phosphorus were taken as models for compounds with amino or alkyl groups on phosphorus to show up trends with higher phosphazene systems.

Ab initio calculations of some neutral compounds and their protonated forms were made at the HF/3-21G* level with full optimization of the geometry. The protonation energies, PE(B) of the base B were computed as the heat of the reaction for the proton attachment energies for the protonation equilibrium:

$$\mathrm{B} + \mathrm{H}^+ \rightleftharpoons \mathrm{BH}^+$$
$$\mathrm{PE(B)} = E(\mathrm{H}^+) + E(\mathrm{B}) - E(\mathrm{BH}^+) \qquad (2)$$

TABLE 1: Results of Basicity Calculations of Simple Imines and Their Derivatives at DFT B3LYP/6-311+G, ab Initio 3-21G*, and Semiempirical PM3 Levels of Theory**[a]

base B	B3LYP/ 6-311+G**		3-21G*	PM3
	PA	GB	PE	PA
$H_2C=NH$	207.7	200.1	230.9	201.5
$H_2NCH=NH$	227.8	220.0	254.6	216.2
$MeCH=NH$	218.1	211.3	247.6	207.3
$Me_2C=NH$	226.6	219.8	251.1	212.2
$Me(NH_2)C=NH$	234.8	227.3	260.9	218.6
$(H_2N)_2C=NH$	237.5	230.6	266.8	220.0
$(H_2N)_2Si=NH$	241.1	236.6	272.7	223.0
$(Me_2N)_2C=NH$	248.2	240.7	272.7	266.8
$H_3P=NH$	230.3	223.4	254.6	249.4
$Li_3P=NH$	277.0	270.6	342.8	267.5
$K_3P=NH$	317.6	309.1	318.9	*b*
$H_3P=NMe$	235.8	228.4	259.1	244.6
$H_3P=N$-t-Bu	240.0	232.2	262.0	249.3
$Me_3P=NH$	252.5	243.5	273.1	242.2
$(H_2N)_3P=NH$[c]	249.7	241.1	283.2	233.0
$(Me_2N)_3P=NH$	256.3	249.2	284.9	241.3
$(H_2N)_3P=NMe$	253.8	245.6	284.0	228.5
$(Me_2N)_3P=NMe$	260.3	252.3	291.3	237.6
$(NH_2NH)_3P=NH$	246.0	239.1	293.0	228.3
$H_2O=NH$	229.0	221.1	242.4	211.3
$H_2S=NH$	229.3	221.7	260.8	220.3
$H_3N=NH$	249.7	242.1	272.7	220.3
$Li_3N=NH$	284.2	277.6	302.5	266.8
$K_3N=NH$	281.1	273.6	277.5	*b*
$H_4S=NH$	231.2	223.8	258.9	229.9
$(H_2N)_4S=NH$	241.7	234.9	288.9	226.7
$H_5Cl=NH$	247.9	240.6	278.3	178.2
$(H_2N)_5Cl=NH$	246.0	237.1	278.4	190.5
2	253.1	245.2	278.1	237.6
6	266.1	258.9	300.1	241.7
$H_3P=N-PH_2=NH$	249.6	243.8	284.0	274.6
$H_3P=N-PH_2=NMe$	260.5	253.1	293.5	267.0
$(H_2N)_3P=N-P(NH_2)_2=NH$	271.5	265.0	300.6	254.8
$(H_2N)_3P=CH-P(NH_2)_2=NH$	260.1	253.6	299.0	256.0
$H_3P=(N-PH_2)_2=NH$	253.9	249.4	282.5	285.2
$(H_3P=N)_2P(H)=NH$	262.0	256.1	300.0	291.6
$(H_2N)_3P=N-P(NH_2)[N=P(NH_2)_3]=NH$[d]	273.0	265.5	316.0	269.7
$H_3P=N-P(N=PH_3)_2=NH$	273.9	267.8	313.1	275.0
$H_3P=N-PH_2=N-P(N=PH_3)_2=NH$	271.3	266.8	322.0	310.7

[a] Basicities (GB), proton affinities (PA), and protonation energies (PE) in kcal/mol (1 kcal = 4.184 kJ). [b] The PM3 method has not been parametrized for potassium. [c] The complex formation of this compound with lithium cation is predicted to be characterized by Li^+ basicity (LCB) value 59.4 kcal/mol and by Li^+ affinity (LCA) 65.8 kcal/mol (for the complex of Li^+ with $(H_2N)_2P=NH$, $E = -572.1073$ au, $H = -571.9982$ au, and $G = -572.0385$ au; for Li^+, $E = -7.2849$ au, $H = -7.2826$ au, and $G = -7.2977$ au). [d] B3LYP/6-31+G* results.

where $E(H^+) = 0$ and $E(B)$ and $E(BH^+)$ are total energies of the base and its protonated form, respectively. No corrections for zero-point vibrational energies were introduced.

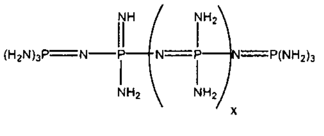
Comparison of results obtained in the current work at HF/3-21G* and B3LYP/6-311+G** levels indicates that there is a reasonable correlation between protonation energies obtained at those different levels of theory ($R^2 = 0.889$). There is also a systematical difference between those methods as the slope (1.14) and intercept (−14.85) of the regression line differ from their ideal values (1 and 0, respectively).

Semiempirical calculations were performed at the PM3 level of theory.[20] In that case, the heat of formation of the proton was taken equal to 365.7 kcal/mol. It was demonstrated[21] that the PM3 method gives rough estimates of the gas-phase proton affinities of a wide variety of neutral molecules with 13 kcal/mol average absolute error in calculated proton affinities and square of correlation coeficient $R^2 = 0.890$ between calculated and experimental proton affinities.

TABLE 2: Results of Basicity Calculations of Simple Imines and Their Derivatives on ab Initio 3-21G* and Semiempirical PM3 Levels of Theory[a]

Base B	3-21G*	PM3
	PE	PA
$(Me_2N)_3P=N$-t-Bu	286.9	240.8
$Me_3P=N-P(Me)_2=NH$	293.5	267.0
$Me_3P=CH_2-P(Me)_2=NH$	300.3	274.5
$(Me_2N)_3P=N-P(NMe_2)_2=NMe$	307.2	252.9
$(Me_2N)_3P=N-P(NMe_2)_2=N$-t-Bu	304.5	264.4
$(H_3P=N\text{-})_2P(H)=NH$	300.0	291.6
$(H_2N)_3P=[N-P(NH_2)_2]_2=NH$	305.5	260.6
$(H_2N)_3P=[CH-P(NH_2)_2]_2=NH$	315.7	272.6
$[(H_2N)_3P=CH]_2P(NH_2)=NH$	316.9	276.8
$Me_3P=(N-PMe_2)_2=NH$	304.4	276.6
$(Me_3P=N\text{-})_2P(Me)=NH$	309.5	283.6
$(Me_3P=CH\text{-})_2P(Me)=NH$	308.1	292.1
$Me_3P=CH-PMe_2-CH=PMe_2=NH$	306.9	284.8
$Me_2N-P[\text{-}N=P(NMe_2)_3]_2=N$-t-Bu	320.8	269.5
$[(H_2N)_3P=N]_3P=NH$	321.0	275.0
$(Me_3P=N)_3P=NH$	321.1	296.3
$[(H_2N)_3P=CH]_3P=NH$	323.6	287.8
$[(Me_2N)_3P=N]_3P=N$-t-Bu	327.1	280.0
11(1)[b]		289.3
10(2)[b]		281.5
10(3)[b]		293.4
11(2)[b]		293.7
10(4)[b]		297.0
11(3)[b]		302.2
$\{(H_2N)_3P=N-P(NH_2)_2=N\}_3P=NH$		302.0
10(5)[b]		303.2
11(5)[b]		310.6
$\{(H_2N)_3P=N\text{-}[P(NH_2)_2=N]_2\}_3P=NH$		318.7
11(8)[b]		319.3
11(16)[b]		327.4
11(18)[b]		317.0

[a] Protonation energies (PE) and proton affinities (PA) in kcal/mol (1 kcal = 4.184 kJ). [b] See the scheme below for explanations.



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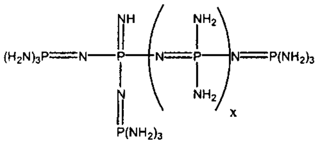

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Results and Discussion

A summary of the results is given in Tables 1−5. Two major groups of factors contibute most importantly to the extraordinary base strength of phosphazene bases:

(a) The stabilization of the highly polarizable protonated form, e.g., t-BuP_4H^+, by inductive effects (field effect of substituents) and delocalization of the charge over a rather extensive, sterically favorable conjugated system.

(b) The relatively high weight of the “anionoid” internal ion-pair like zwitterionic resonance structures with the extensive localization of charges of the type (B) in the neutral phosphazene base (A; see Scheme 2).

The resonance structure (B) could be considered as the substitution product of the group X in XNH^- anion by $(R_1R_2N)_3P^+$ group. This would lead to the electrostatic stabilization of the resulting anionic species and makes it less basic than NH_2^- anion (X = H) where the N atom carries the most of the negative charge. It follows that any replacement of H atom in NH_2^- by electron accepting or/and positively charged groups (like $(NH_2)_3P^+$) will increase the stability and reduce the basicity of the “naked” basicity center NH_2^-. Therefore, with the probable exception of electron donor groups (NH_2, etc.) or

TABLE 3: Results of Basicity Calculations of Simple Ylides and Their Derivatives at DFT B3LYP/6-311+G**, ab Initio 3-21G*, and Semiempirical PM3 Levels of Theory[a]

	B3LYP/ 6-311+G**		3-21G*	PM3
base B	PA	GB	PE	PA
$H_2C=CH_2$	163.6	156.1	162.7	159.8
$(H_2N)_2C=CH_2$	244.2	237.4	266.5	224.2
$(H_2N)_2Si=CH_2$	251.4	244.4	272.6	265.8
$Me_2C=CH_2$	197.2	191.2	204.3	185.1
$Me_2Si=CH_2$	233.4	226.6	246.6	227.7
$H_3P=CH_2$	252.2	244.6	268.4	262.0
$MePH_2$	203.6	196.1	210.4	241.5
$Li_3P=CH_2$	295.3	287.9	292.4	247.6
$K_3P=CH_2$	315.6	305.7	320.2	*b*
$(H_2N)_3P=CH_2$[c]	264.0	256.8	298.9	242.7
$(H_2N)_3P=CMe_2$	272.0	264.3	304.3	251.2
$(Me_2N)_3P=CH_2$	274.5	267.8	298.9	257.3
$(H_2NNH)_3P=CH_2$	268.9	261.3	292.0	254.8
$Me_3P=CH_2$	271.9	264.1	288.2	259.8
$(H_2N)_4S=CH_2$	258.9	251.9	316.4	239.8
$Me_3N=CH_2$	289.1	279.7	316.4	259.9
$H_3N=CH_2$	276.9	270.7	303.4	246.3
$Li_3N=CH_2$	296.6	287.2	330.3	293.8
$K_3N=CH_2$	279.7	269.1	285.4	244.0
$H_2O=CH_2$	262.2	253.5	285.4	244.0
$H_2S=CH_2$	250.9	243.4	269.0	238.5
$H_4S=CH_2$	236.7	230.8	242.4	242.7
$H_5Cl=CH_2$	258.5	250.3	290.3	164.5
$(H_2N)_5Cl=CH_2$	256.1	247.5	292.6	d
$H_3P=N-PH_2=CH_2$	267.3	260.5	293.3	284.4
$(H_2N)_3P=N-P(NH_2)_2=CH_2$	282.1	275.7	312.6	268.8
$(H_2N)_3P=CH-P(NH_2)_2=CH_2$	280.5	273.9	312.8	271.0
4	249.4	242.3	268.0	234.4
7	280.9	273.3	314.9	261.9
$(H_3P=N\text{-})_2P(H)=CH_2$	280.7	275.2	317.5	303.5
$H_3P=N-PH_2=N-PH_2=CH_2$	277.2	270.4	299.4	296.1
$[(H_2N)_3P=N\text{-}]_2P(NH_2)=CH_2$[e]	295.0	288.6	331.8	288.4
$(H_3P=N\text{-})_3P=CH_2$	294.0	288.7	332.2	321.7
$H_3P=N-PH_2=N-P(-N=PH_3)_2=CH_2$	291.3	290.4	314.7	326.3

[a] Basicities (GB), proton affinities (PA), and protonation energies (PE) in kcal/mol (1 kcal = 4.184 kJ). [b] The PM3 method has not been parametrized for potassium. [c] The complex formation of this compound with lithium cation is calculated to have LCB value 48.7 kcal/mol ($E = -556.0008$ au, $H = -555.8821$ au, and $G = -555.9245$ au). [d] The protonated form decomposes at PM3 level. [e] B3LYP/6-31+G* results.

electropositive substituents whose introduction, e. g., due to the repulsion of the $\alpha-\alpha$ lone electron pairs, leads to destabilization of the anion, the intrinsic basicity of the phosphorus imine family cannot exceed that for the parent base RNH^-. Similar resonance structures could be written also for the ylide family (see Scheme 3). The nature of the chemical bonding in ylide compounds of different elements (N, P, As, S, etc.) has been extensively studied and discussed.[7,12,22]

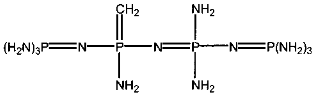
Oxygen and nitrogen atoms are not able to form four and five covalent bonds, respectively. Therefore, in the case of N and O ylides, the double bonding between the heteroatom and carbon is negligible, and hence, the O^+-C^- and N^+-C^- bonds are relatively long (1.6−1.8 Å) and nearly ionic, e. g., $H_3N^+-{}^-CH_2$ or $H_2O^+-{}^-CH_2$. However, the P and S atoms in ylides are able to expand their valence shell up to 10 or 12 electrons, respectively. Therefore, in contrast to the N and O ylides, they are able to form a double bond between P or S atom and ylide carbon atom which results in a significant stabilization, lower polarity, shorter P−C, S−C, etc. bond lengths, and also, at a fixed X^1, the lower basicity of the ylides of P and S as compared with ylides of nitrogen and oxygen. To some extent, the effect of higher ionicity of the O^+-C^- and N^+-C^- bonds as compared to those of the P^+-C^- and S^+-C^- bonds is compensated by the basicity reducing effect of higher electronegativity of O and N atoms as compared with P and S atoms.

Using the same considerations as in the case of phosphorus imines and considering methanide anions (XCH_2^-, where X =

TABLE 4: Results of Basicity Calculations of Simple Ylides and Their Derivatives on ab Initio 3-21G* and Semiempirical PM3 Levels of Theory[a]

	3-21G*	PM3
base B	PE	PA
$Ph_3P=CH_2$	296.1	267.7
$(Me_2N)_3P=CH_2$		278.0
$Me_3P=N-PMe_2=CH_2$	310.3	280.7
$(Me_2N)_3P=N-P(NMe_2)_2=CH_2$	319.0	275.7
$(H_3P=CH\text{-})_2P(H)=CH_2$	294.8	312.7
$(H_2N)_3P=N-P(NH_2)_2=N-P(NH_2)_2=CH_2$	326.3	280.3
$[(H_2N)_3P=CH\text{-}]_2P(NH_2)=CH_2$	339.0	290.0
$(Me_3P=N\text{-})_2P(Me)=CH_2$	328.4	296.5
$(H_2N)_3P=CH-P(NH_2)_2=CH-P(NH_2)_2=CH_2$	327.5	285.9
$(H_2N)_3P=[N-P(NH_2)_2]_3=CH_2$	324.0	281.4
$Me_3P(=CH-PMe_2)_2=CH_2$	315.8	308.2
12[b]	324.1	293.3
$[(H_2N)_3P=N]_3P=CH_2$	345.1	296.5
$[(H_2N)_3P=CH]_3P=CH_2$		282.4
$(Me_3P=N)_3P=CH_2$	350.0	311.8
$(Me_3P=CH)_3P=CH_2$	334.9	320.7
$Me_3P(=CH-PMe_2)_3=CH_2$	333.6	308.3
13(1)[b]	351.3	303.9
$(H_2N)_3P[=N-P(NH_2)_2]_4=CH_2$	326.4	288.8
13(2)[b]		308.6
13(3)[b]		318.2
13(5)[b]		318.5
$[(H_2N)_3P=N-P(NH_2)_2=N\text{-}]_3P=CH_2$		316.6
$\{(H_2N)_3P=N\text{-}[P(NH_2)_2=N]_2\text{-}\}_3P=CH_2$		331.3
13(16)[b]		328.4
13(19)[b]		330.0
$Me_3N=CH_2$	316.4	259.9
$H_3N=CH_2$	303.3	246.4

[a] Protonation energies (PE) and proton affinities (PA) in kcal/mol (1 kcal = 4.184 kJ). [a] See the scheme below for explanations.



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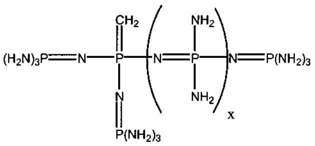

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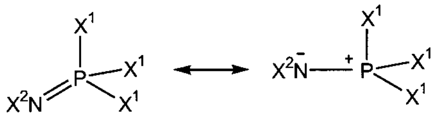
TABLE 5: Results of Basicity Calculations of Some Phosphines at DFT B3LYP/6-311+G**, ab Initio 3-21G*, and Semiempirical PM3 Levels of Theory[a]

	B3LYP/ 6-311+G**		3-21G*	PM3
Base B	PA	GB	DPE	PA
PH_3	187.4	180.5	193.8	248.7
Li_3P	285.3	278.5	297.7	247.7
K_3P	318.8	311.7	338.0	*b*
Me_3P	226.9	219.3	232.3	227.2
$(H_2N)_3P$	225.9	218.1	253.9	202.4
$(Me_2N)_3P$	237.8	230.9	262.8	216.2
$H_3P=N-PH_2$	224.6	217.3	242.8	273.2
$H_3P=N-P(NH_2)_2$	241.6	234.3	270.3	241.0
$Me_3P=N-PMe_2$	252.8	245.1	272.2	252.2
$(H_2N)P(N=PH_3)_2$	252.4	245.8	289.0	265.0
$P(-N=PH_3)_3$	265.1	258.3	303.3	291.7
$(H_2N)_3P=N-P(NH_2)_2$	253.6	245.6	284.5	230.0
5	252.4	244.6	284.9	217.4

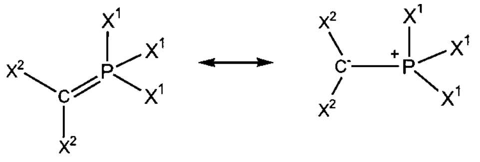
[a] Protonation energies (PE) and proton affinities (PA) in kcal/mol (1 kcal = 4.184 kJ). [b] The PM3 method has not been parametrized for potassium.

SCHEME 2



A B

SCHEME 3



C D

H) as the formal parent bases for the ylides' family, one should expect that, as a rule, no ylide bases can exist whose intrinsic basicity would exceed that of methanide anion (with the possible exception if X is the electron donor or strongly electropositive [e. g., alkali-metal atom] substituent).

One might assume that the difference of the basicities of the hypothetical limiting structures **B** and **D** of the parent molecules of the representatives of ylide and imine families will be, to some extent, "memorized" and expressed also by the respectively higher basicity values of ylides XCH_2 as compared with the imines XNH with the common substituent X.

The present calculations at different levels of theory (B3LYP/6-311+G**, HF/3-21G*, and PM3) provide evidence (see Figures 1−3) that this prediction is expected to be realized at least in the case of some simple model systems. For model compounds with $X_1 = H$, NH_2 and $X_2 = H$, one can see from Figure 1 that in all examples the calculated gas-phase basicities (DFT level) or protonation energies (HF/3-21G*) and enthalpies (PM3 level) of representatives of phosphorus imine and phosphorus ylide families with a fixed substituent X are expected to increase asymptotically with the increase of the number n of phosphorus atoms in the system. In all cases, at a fixed n value for $n \geq 1$, the higher basicity and PE values for the corresponding phosphorus ylides is predicted. The calculated differences between the basicities and PE of the respective ylides and imines at a fixed n value are evident from Figures 1−3, vary in the range from 9 to 21 kcal/mol, and depend on the nature of X^1 and used level of calculations. At the DFT B3LYP/6-311+G** level of theory, the gap between calculated basicitites of comparable ylides and imines is larger for compounds with $X^1 = H$ than for bases with $X_1 = NH_2$.

Influence of the Number of Phosphorus Atoms on the Basicity of Phosphorus Imines and Ylides. From Figure 3 one can extrapolate that the "magic" 300 kcal/mol intrinsic basicity margin for the organic model superbases will be reached at $n = 5$ or 6 for phosphorus ylides with $X^1 = NH_2$ and $X^2 = H$ and for the respective phosphorus imines with the same substituents at $n = 7−10$. For the ylides with $X^1 = H$ and $X^2 = H$, the same basicity level will be predicted to be reached at $n = 8$ or 9, whereas phosphorus imines with the same substituents are not expected to reach that basicity value until $n \geq 10$.

The results of the PM3 calculations include phosphazene and phosphorane bases with up to 22 P atoms and are in a reasonably good agreement with those using DFT B3LYP at 6-311+G** level.

The DFT B3LYP/6-311+G** calculations of even the simplest model compounds ($X^1 = H$ and $X^2 = H$) are available only for up to five P atoms. Therefore, to monitor the general trends of comparative changes of PE values for phosphorus ylides and imines at higher numbers of phosphorus atoms, the semiempirical PM3 calculations of the dependence of PA of phosphorus imines A and phosphorus ylides having the asymmetric branching at the second atom of phosphorus B upon the total number of phosphorus atoms n were carried out up to 22 atoms of phosphorus. Those calculations reveal that the limiting PA values (at a very large n) reach ca. 330 kcal/mol for phosphazene ylides and 315−320 kcal/mol for phosphazene imines.

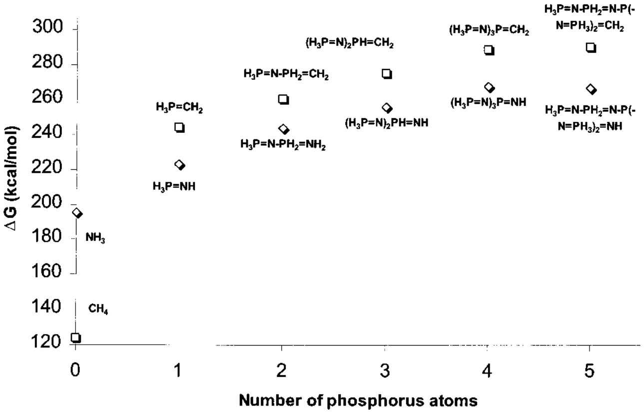


Figure 1. Dependence of the gas-phase basicity of phosphorus imines (rhombs) and phosphorus ylides (squares) at DFT B3LYP/6-311+G** level ($X^1 = X^2 = H$) on the number of phosphorus atoms.

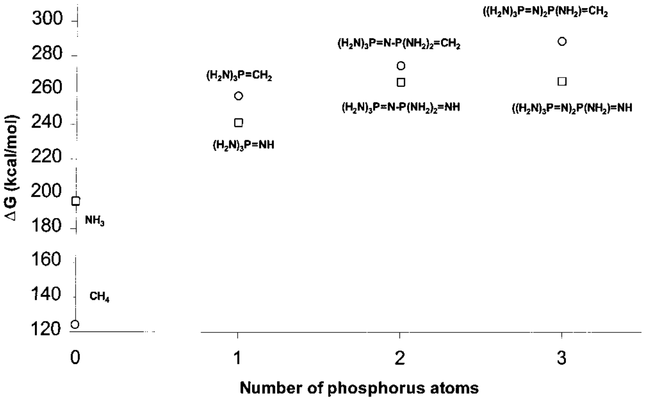


Figure 2. Dependence of the gas-phase basicity of phosphazenes (squares) and phosphorus ylides (circles) at the DFT B3LYP/6-311+G** level ($X^1 = NH_2$, $X^2 = H$) on the number of phosphorus atoms.

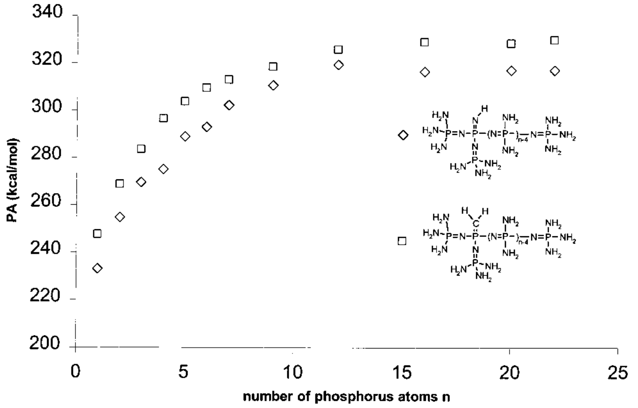


Figure 3. Dependence of the proton affinity of phosphazenes and phosphorus ylides (at the PM3 level) on the number of phosphorus atoms.

At the same time, PM3 calculations of phosphorus imines, e.g., $\{(H_2N)_3P{=}N{-}[P(NH_2)_2{=}N]_m\text{-}\}_3P{=}NH$, where $m = 1$ or 2 and phosphorus ylides $\{(H_2N)_3P{=}N{-}[P(NH_2)_2{=}N]_m\text{-}\}_3\text{-}P{=}CH_2$, where $m = 1$ or 2, having symmetrical branching at the basicity center $=NH$ or $=CH_2$, reveal that even higher PA values could be reached (e.g., for imines 302.0 and 318.7 kcal/mol respectively with $m = 1$ and 2 and for phosphorus ylides 316.6 and 331.3 kcal/mol for m values 1 and 2, respectively). This means that, for these two series of species carrying respectively 7 and 10 phosphorus atoms, the gap between calculated PA values for ylides and imines is still 12.6−14.6 kcal/mol which is only slightly less than for similar compounds $[(H_2N)_3P{=}N]_3P{=}NH$ and $[(H_2N)_3P{=}N]_3P{=}CH_2$ with four atoms of phosphorus where ΔPA is 21.5 kcal/mol. In solution, the experimentally determined gap between basicities of $[(Me_2N)_3P{=}N]_3P{=}CH_2$ and t-BuP$_4$ is found to be ca. 6 pK_a units or 8 kcal/mol.[23]

Extremely high predicted basicity of organic ylide superbases competes successfully with the most basic inorganic superbases, probably with the only exceptions of Cs_2O and the tripotassium nitride superbase K_3N.[24] According to the DFT B3LYP/6-311+G** calculations,[25] the latter molecule (planar, C_{3V} symmetry, zero dipole moment; the Mulliken population analysis gives −1.83 charges on N and 0.61 charges on K) and its protonated form (C_{3V} symmetry; the Mulliken population analysis gives −1.84 charges on N, 0.15 charges on H, and 0.90 charges on K) are predicted to be stable. The GB value of K_3N on this level of theory is calculated to be 340.7 kcal/mol which, to the best of our knowledge, exceeds any other calculated basicity value for any neutral inorganic or organic superbase.

Influence of the Substituents X^1 and X^2 at the Phosphorus Atom and Nitrogen of the Imino Group of Phosphorus Imines. Already the simple imines,[26] e.g., formaldimine ($H_2C{=}NH$), are bases of moderate strength in the gas phase ($GB_{exp} = 197.0$ kcal/mol and $GB_{calc} = 200.1$ kcal/mol (DFT/6-311+G** level) and $PA_{exp} = 205.5$ kcal/mol and $PA_{calc} = 207.7$ kcal/mol). The consecutive replacement of two $=CH_2$ hydrogen atoms by NH_2 groups is expected to lead to a rather significant increase of basicity. So, for $H_2NCH{=}NH$, the calculated at DFT/6-311+G** level basicity increase is 19.9 kcal/mol, whereas the calculated GB value for guanidine equals 230.6 kcal/mol (30.5 kcal/mol stronger than $H_2C{=}NH$, see also ref 21). In its turn, tetramethylguanidine (TMG) is calculated to be, by ca. 10 kcal/mol, more basic than guanidine in a reasonable agreement with the experimental findings of Raczynska et al.[4−6] The primary reason for the strong basicity of guanidines is the high stability of the guanidinium cations which is due to the so-called "Y-delocalization"[6,27,28] of the three lone pairs of the amino or substituted amino groups of the guanidinium system. The replacement of one hydrogen atom of $=CH_2$ group of formaldimine by methyl group is expected to increase the basicity by 11.2 kcal/mol whereas the simultaneous introduction of amino and methyl groups (acetamidine) results in a 27.2 kcal/mol increase of the basicity of $H_2C{=}NH$.

The replacement of the $=CH_2$ group of formaldimine by the double-bonded $=PH_3$ fragment is calculated to increase the basicity of the system to ca. 223 kcal/mol level. The substitutions of the hydrogen atom of the imino group in (hypothetical) $H_3P{=}NH$ by Me and t-Bu groups are expected to increase the basicity of the resulting species by 5.0 and 8.8 kcal/mol, respectively, thus reaching or exceeding the basicity level of guanidine and TMG.[1,27] Similar N-alkyl substituent effects have been previously noticed for TMG, $H_2C{=}NH$, and $MeCH{=}NH$.[1,4−6,26]

TABLE 6: Comparison of the Effects of NH_2 and CH_3 Groups on the Protonation Energies (in kcal/mol) of Simple Phosphorus Imines ($X^1 = NH_2$ or CH_3 and $X^2 = H$), HF/3-21G* Results

n^a	NH_2 substituents	CH_3 substituents	Δ
1	283.2	273.1	10.1
2	300.6	293.5	7.1
3^b	316.0	309.5	6.5
4^b	321.0	321.1	0.1

[a] n is the number of phosphorus atoms. [b] The $=NH$ group is at the second phosphorus atom.

The substitution of the three hydrogen atoms of the $=PH_3$ group in $H_3P{=}NH$ by amino groups is calculated to increase additionally the basicity by 17.7 kcal/mol, to 241.1 kcal/mol, well beyond the basicity level of guanidine or comparable to the calculated value for TMG. Even larger (21.2 kcal/mol) is the effect of substitution of all H atoms for NH_2 groups at P atoms in $H_3P{=}N{-}PH_2{=}NH$.

Somewhat suprisingly, the replacement of hydrogen atoms of the $=PH_3$ group in the $H_3P{=}NH$ system by Me groups is calculated to increase the basicity of the resulting species even more so, to 243.5 kcal/mol, i.e., to the level of 7-isopropyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (ITBD).[4,5] The results of DFT B3LYP calculations using the 6-311+G** basis set show that $(H_2N)_3P{=}NH$ is by 2.4 kcal/mol a weaker base than $Me_3P{=}NH$ but that the latter is by 5.7 kcal/mol weaker a base than $(Me_2N)_3P{=}NH$. Titration of trialkylphosphane imine bases in MeCN indicate that they are slightly less basic than their dialkylamino-substituted counterparts.[29] PM3 calculations support this result, whereas ab initio calculations at the 3-21G* level predict somewhat stronger basicity for the NH_2 derivatives as compared with their methyl-substituted counterparts (see Table 6). Starting with the phosphazenes including four phosphorus atoms, the effects of these substituents are predicted to lead to practically the same calculated protonation energies.

Additional replacement of amino groups in $(H_2N)_3P{=}NH$ by dimethylamino groups results in a known HP$_1$ superbase[8,9] with a predicted gas-phase basicity value of 249.2 kcal/mol (or 8.5 kcal/mol stronger than the calculated basicities for $(H_2N)_3\text{-}P{=}NH$ and TMG) which already goes beyond the so far established continuous basicity ladder[1,4,5] for acyclic and cyclic guanidines, vinamidines, etc.

Taking into account the expected basicity increase due to the introduction of N-alkyl substituents into HP$_1$ (vide supra), the predicted basicity of these simple easily available or commercial phosphazene superbases (e.g., MeP$_1$, t-BuP$_1$, etc.) should be placed around 255−260 kcal/mol. The basicity of MeP$_1$ calculated in this work (252.3 kcal/mol) supports this prediction.

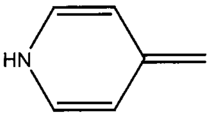
However, our calculations show that even much stronger basicity is expected for the hypothetic derivative of $H_3P{=}NH$ where all of the hydrogen atoms of the $H_3P{=}$ group are replaced by alkali-metal atoms, e.g., Li, Na, K, etc. The calculated GB values for the protonation of Li_3PNH and K_3PNH are 270.6 and 309.1 kcal/mol, respectively, that is by 47.2 and 85.7 kcal/mol more basic than their unsubstituted predecessor.

The calculated structures for the neutral forms ($Li_3P{=}NH$ and K_3PNH) are characterized by a strong intramolecular bond between two of three alkali-metal atoms and nitrogen of the imino group which significantly reduces the basicity of the NH group. The Mulliken charge on the basicity center, N atom of the imino group, is relatively modest: −0.4 units of elementary charge. In the protonated form, the N atom of the NH_2+ group is coordinated only to one Li atom. The extra stabilization of the neutral base relative to its protonated form by the alkali-metal atoms is probably responsible for the reduction of the basicity of $Li_3P{=}NH$ and $K_3P{=}NH$ as compared with that of the Li_3P and K_3P molecules (vide infra).

The replacement of the $H_3P{=}$ group in $H_3P{=}NH$ by the $H_3N{=}$ group is expected to lead to a much stronger base, $H_3N{=}NH$ (high-energy tautomeric form of hydrazine), whose GB is calculated to be 242.1 kcal/mol, roughly equal to the basicity for $(H_2N)_3P{=}NH$ or $Me_3P{=}NH$ (see Table 1, DFT B3LYP/6-311+G** calculations) and with a relatively long N−N bond (1.7 Å).

Similar to the case of trilithium and tripotassium derivatives of $H_3P{=}NH$, $Li_3N{=}NH$ (GB=277.6 kcal/mol) and $K_3N{=}NH$ (GB=273.6 kcal/mol) are expected to be much stronger bases than their unsubstituted analogue $H_3N{=}NH$. However, the Mulliken population analysis shows that, differently from the alkali-metal substituted derivatives of $H_3P{=}NH$, the density of the negative charge on the nitrogen of the imino group of tri-alkaline-metal substituted imines of ammonia is, in contrast to the alkyl substituted derivatives, only slightly negative (−0.28 to −0.39), whereas Mulliken charges on Li and K atoms are only around +0.15 to +0.16 charge units. Especially in the case of K_3NNH, the calculated N−N bond distance is extremely short: −1.27 Å. Similar to the calculated geometries of $Li_3P{=}NH$ and $K_3P{=}NH$, the neutral forms of $Li_3N{=}NH$ and $K_3N{=}NH$ are also extra-stabilized by the interaction of the lone pairs of the nitrogen atom of the imino group with alkali-metal atoms. In the protonated forms $Li_3N{=}NH_2^+$ and $K_3N{=}NH_2^+$, this intramolecular stabilization is weaker which causes very significant reduction of the calculated basicity of $Li_3N{=}NH$ and $K_3N{=}NH$ as compared with the molecules of Li_3N and K_3N.[24]

The present simple DFT B3LYP/6-311+G** level model calculations are also in agreement with the suggestions[14] about the significant basicity increasing effects caused by the replacement of the $={CH_2}$ group in $H_2C{=}NH$ by much better and more extensive cation stabilizing fragment **1**: The GB value of protonation of the resulting compound **2** is already as much as 245.2 kcal/mol, i.e., in the superbasicity region between the values for $(H_2N)_3P{=}NH$ and $(Me_2N)_3P{=}NH$.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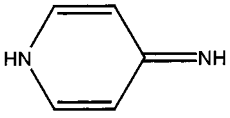
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Effect of Replacement of the −N= Bridge for the −CH= Bridge on Protonation Energies of Phosphorus Imines and Ylides. Both in the case of phosphorus imines and in the case of phosphorus ylides with two phosphorus atoms, DFT calculations at the 6-311+G** basis seem to evidence that the replacement of the −N= bridge by the isoelectronic −CH= bridge somewhat decreases the basicities of the corresponding NH_2-substituted species $(NH_2)_3P{=}N{-}P(NH_2)_2{=}NH$ and $(NH_2)_3P{=}N{-}P(NH_2)_2{=}CH_2$ respectively by 11.4 and 1.8 kcal/mol. At the same time, semiempirical PM3 and low level ab initio (HF/3-21G*) calculations (see Table 7) give controversal results from which it is impossible to draw general conclusions. Titrations in MeCN solution show a small increase (0.44 p*K* units or 0.6 kcal/mol) of basicity on replacement of the −N= bridge in EtP_2 by the −CH= bridge.[29]

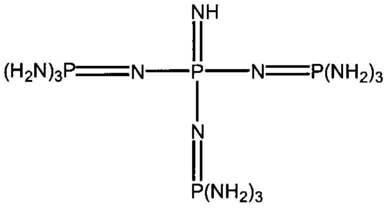
Effect of Branching on Basicity of Phosphazene Imines and Phosphazene Ylides. It was experimentally demonstrated[8,9] that the pK_a's of conjugated acids of branched-chain phosphazene imines (e.g., t-BuP_4, t-BuP_5, etc.) are always higher (higher basicity of the conjugated base) than those of their linear-chain counterparts.

These findings are fully supported by the present DFT B3LYP calculations at the 6-311+G** basis and ab initio (HF/3-21G*) and PM3 calculations which show that the stability of the linear-chain bases is always higher than that of their branched (concerning the position of the imino group) counterparts. At the same time, the protonation energies (or basicities) of the branched-chain bases at a fixed number of phosphorus atoms are higher than that of the linear-chain bases.

So, in the case of P_3 bases $(H_2N)_3P{=}[N{-}P(NH_2)_2]_2{=}NH$ and $[(H_2N)_3P{=}N]_2P(NH_2){=}NH$, the former species is calculated (HF/3-21G*) to be by 11.5 kcal/mol more stable than its branched counterpart. As far as those two bases have the same protonated form, the latter has by the same increment a higher protonation energy. Practically the same results are gotten using the PM3 method (the linear-chain isomer is calculated to be by 9.1 kcal/mol more stable).

DFT calculations at the 6-311+G** basis fully confirm these findings for the simpler model compounds $H_3P{=}N{-}P(H_2){=}NP(H_2){=}NH$ and $H_3P{=}N{-}P(H)({=}NH)\text{-}NPH_3$. The former structure is by 6.7 kcal/mol lower (more stable) in free energy and by the same margin less basic than its branched counterpart.

Similar results characterize the stability of the isomers and their relative stability in the case of P_4 phosphazene imines (HF/3-21G*). Here the linear 1-imino-isomer $(H_2N)_3P{=}[N{-}P(NH_2)_2]_3{=}NH$ is by 8.5 kcal/mol (PM3 gives 8.8 kcal/mol) more stable than the 2-imino isomer. At the same level of theory, the latter is in its turn by 9.9 kcal/mol more stable than the branched structure **3** $[(H_2N)_3P{=}N{-}]_3P{=}NH$.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The protonation energy of the latter is expected to be, by 5.2 kcal/mol, higher than for linear 2-imino-isomer and, by 13.7 kcal/mol, higher than the same quantity for the 1-imino isomer.

Similar behavior is characteristic also for the relative stabilities and protonation energies of the phosphazene ylides. So, as evidenced by DFT/6-311+G** calculations, the linear P_3 ylide $H_3P{=}N{-}PH_2{=}N{-}PH_2{=}CH_2$ is by 4.8 kcal/mol less basic than the 2-CH_2 isomer.

Similarly, the linear $(H_2N)_3P{=}N{-}P(NH_2)_2{=}N{-}P(NH_2)_2{=}N{-}P(NH_2)_2{=}CH_2$ isomer is predicted to have by 0.1 kcal/mol at 3-21G* level and 11.9 kcal/mol by PM3 calculations lower protonation energy than its 2-$={CH_2}$ counterpart. The latter is calculated to be by 16.1 kcal/mol (5.3 kcal/mol at PM3 level) more stable than the branched isomer $[(H_2N)_3P{=}N{-}]_3P{=}CH_2$ whose protonation energy, in its turn, is by 3.2 kcal/mol higher than that of the linear 2-CH_2 isomer.

pK_a vs PA of Phosphorus Imines. In earlier works[8,9,11] of some of us, the pK_a values of several phosphazene superbases with different number of phosphorus atoms were determined in acetonitrile solution. It was also shown[10,11,13,30] that substituent effects on the basic pK_a's within the series of substituted aromatic or aliphatic amines are relatively weakly sensitive toward solvent effects. So, only a modest change of the relative

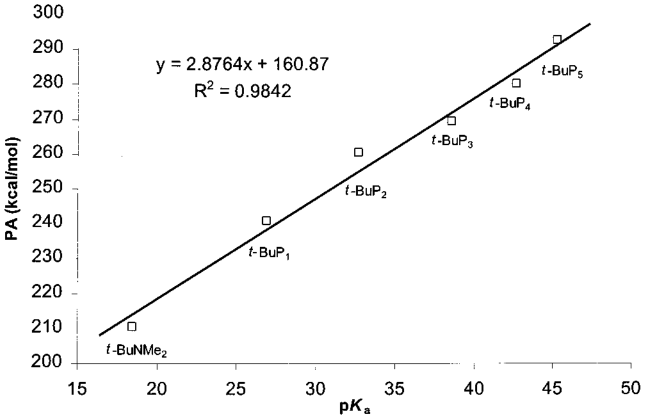


Figure 4. Correlation of calculated (PM3) protonation energies of t-Bu phosphazene bases with the different number of phosphorus atoms with their pK_a values in acetonitrile solution.

basicity of substituted anilines and aliphatic amines takes place when transfer from aqueous solution into DMSO, into acetonitrile, or even into the gas-phase takes place. No such comparison has so far been available for the pK_a values of substituted phosphazenes upon transfer from the gas-phase into solution (e.g., MeCN).

In the present work, an attempt was made to compare the semiempirically (PM3) calculated PA values for the series consisting of t-BuP$_1$, t-BuP$_2$, t-BuP$_3$, t-BuP$_4$, and t-BuP$_5$ with the respective experimental pK_a values in acetonitrile solution. The point for the so-called "P$_0$" phosphazene, t-BuNMe$_2$, which contains no phosphorus atoms was also included for comparison (see Figure 4).

The reasonably good correlation

$$\Delta H(\mathrm{PM3}) = 160.9 + 2.88[\mathrm{p}K_a(\mathrm{MeCN})]R^2 = 0.984 \quad (3)$$

shows that the sensitivity ($b/2.3RT$) of this reaction series toward the substituent effects decreases 2.2 times upon changing the gas phase into acetonitrile solution.

Phosphorus Ylides: The Substituent Effects of X^1 at the Phosphorus Atom and X^2 at the Double-Bonded Carbon Atom. The simplest hypothetical phosphorus ylide $H_3P{=}CH_2$ can be formally derived by replacement of the $=CH_2$ group in ethene by the definitely less electronegative the $=PH_3$ group. $H_3P{=}CH_2$ is a thermodynamically unfavorable tautomeric form of methyl phosphine, $MePH_2$. The latter is calculated to be (B3LYP/6-311+G**) by 48.5 kcal/mol more stable than $H_3P{=}CH_2$ (see Table 3). The calculated basicity of ethene at the DFT B3LYP/6-311+G** level is 156.1 kcal/mol. At the same level of theory, the predicted intrinsic basicity of $H_3P{=}CH_2$ as $=CH_2$ base is 244.6 kcal/mol which is practically equal to the experimentally determined basicity of the most basic guanidine superbase ITBD.[4,5]

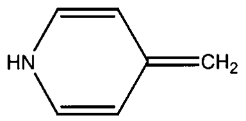
The ylide analogue of guanidine, $(H_2N)_2C{=}CH_2$, the tautomeric form of acetamidine, $MeC({=}NH)NH_2$, is predicted to be by 6.8 kcal/mol a stronger base than guanidine (230.6 kcal/mol) and by 10.1 kcal/mol more basic than acetamidine itself.

Differently from the situation in the series of $P_1{=}NH$ bases the substitution of two methyl groups into ethene leads to isobutene $Me_2C{=}CH_2$ which is calculated to be by 46.2 kcal/mol less basic than $(H_2N)_2C{=}CH_2$.

The simultaneous replacement of three hydrogen atoms of the PH_3 group by NH_2 groups in $H_3P{=}CH_2$ is calculated to increase the basicity of the corresponding P$_1$ ylide by 12.2 kcal/mol to 256.8 kcal/mol, well beyond the limits of the so far existing continuos basicity scale.[1] Similar is the effect (15.2 kcal/mol) of replacement of five hydrogen atoms at phosphorus atoms for the NH_2 group in $H_3P{=}N{-}PH_2{=}CH_2$.

The substitution of the amino groups in $(H_2N)_3P{=}CH_2$ for dimethylamino substituents results in additional calculated basicity increase of 11.0 kcal/mol to GB = 267.8 kcal/mol which is similar to the behavior of the corresponding P$_1$ imines (vide supra). However, the resulting calculated basicity of $(Me_2N)_3P{=}NH$ is by 18.6 kcal/mol lower than in case of $(Me_2N)_3P{=}CH_2$.

The replacement of both hydrogen atoms of the double-bonded $=CH_2$ basicity center in $(H_2N)_3P{=}CH_2$ by methyl groups is expected to result in 7.5 kcal/mol basicity increase (GB of the $(H_2N)_3P{=}CMe_2$ is expected to be 264.3 kcal/mol) which is somewhat larger than a similar effect due to the *N*-methylation of the $=NH$ group in P$_1$ phosphorus imides (vide supra). Assuming the same effect of introduction of two methyl groups into $(Me_2N)_3P{=}CH_2$ leads to the estimated gas-phase basicity value of 275.3 kcal/mol for a recently introduced[31] novel superbase, $(Me_2N)_3P{=}CMe_2$. The latter was in solution (THF) experiments bracketed by its basicity between the respective values of Verkade's bicyclic proazaphosphatrane and t-BuP$_4$ phosphazene imine. However, the inspection of Table 1 shows that the presently estimated intrinsic basicity exceeds somewhat the suggested value for $MeN{=}P(NH_2)_2{-}N{=}P(NH_2)_3$ but should be less or comparable to the basicity of $(Me_2N)_3P{=}N{-}P({=}NH)(NMe_2){-}N{=}P(NMe_2)_3$ which does not contradict to the recent findings.[17]



4

Similar to the replacement of the $=CH_2$ fragment in a simple imine $H_2C{=}NH$, the substitution of the same group by quinoid stabilizing fragment **1** in ethene also yields a highly basic molecule ($=CH_2$ group is the protonation center) **4** whose GB value reaches 242.3 kcal/mol, which is comparable (see also ref 14) to $(H_2N)_3P{=}NH$ or $H_3P{=}CH_2$ but is less basic than its above-mentioned $=NH$ analogue.

CH_3 vs NH_2 at the P Atom. As in the case of the simple phosphorus imines, the transfer from $H_3P{=}CH_2$ to the corresponding $Me_3P{=}CH_2$ derivative is at DFT B3LYP (6-311+G** basis set) level predicted to increase the basicity by 19.5 kcal/mol which is by 7.3 kcal/mol more than the predicted basicity increase (12.2 kcal/mol) due to the transfer from $H_3P{=}CH_2$ to $(H_2N)_3P{=}CH_2$.

PM3 calculations confirm these findings, whereas ab initio 3-21G* calculations predict the effect of the opposite sign.

Phosphorus Ylides vs Nitrogen Ylides. Because of the larger size of the phosphorus atom as compared with that of the nitrogen atom and because of its ability to better delocalize the negative charge of the ylidic carbon atom by expanding its valence shell up to 10 electrons, the phosphorus ylides have relatively shorter P−C distances and lower polarity than their nitrogen counterparts (vide supra). The latter have highly polar, nearly ionic, and relatively long (1.7−1.8 Å) N−C bond distances and a very high negative charge concentration (0.8−0.9 electron charges) on the basicity center, the carbon atom of the $=CH_2$ group. Therefore, the nitrogen ylides are expected to be even more basic than the corresponding phosphorus ylides.[1,12,22a]

Indeed, the DFT calculations at the B3LYP/6-311+G** level show (see Table 3) that the simple nitrogen ylide $Me_3N{=}CH_2$

is expected to be by 22.9 kcal/mol more basic than $(H_2N)_3P{=}CH_2$ and by 15.6 kcal/mol more basic than its closest P analogue, $Me_3P{=}CH_2$.

Even the simplest (hypothetical) nitrogen ylide, $H_3N{=}CH_2$, is predicted to be a very strong base (GB = 270.7 kcal/mol) whose basicity is expected to be comparable to the same quantity for Li_2O[1,3] and to exceed the calculated basicity of $H_3P{=}CH_2$ by 26.1 kcal/mol.

Similar to the above-discussed case of the extraordinarily strong calculated basicities of the hyphothetical trilithium and tripotassium derivatives of $H_3P{=}NH$ and $H_3N{=}NH$, the respective ylides, $Li_3P{=}CH_2$ (GB = 287.9 kcal/mol), $K_3P{=}CH_2$ (GB = 305.7 kcal/mol), $Li_3N{=}CH_2$ (GB = 287.2 kcal/mol), and $K_3N{=}CH_2$ (GB = 269.1 kcal/mol), are also predicted to be very strong bases.

Differently from the unsubstituted, alkyl-substituted, or amino-substituted derivatives of $H_3P{=}NH$ and $H_3N{=}NH$ where the respective nitrogen ylides are found to be stronger bases than P ylides, in the case of their alkali-metal substituted derivatives, this basicity order is calculated to be reversed. Analogously to the case of imides of alkali-metal-substituted phosphine and ammonia, the respective ylides, $Li_3P{=}CH_2$ and $K_3P{=}CH_2$, are characterized by moderate negative Mulliken charges on the carbon atoms and by relatively long (1.9 and 1.7 Å) P−C distances. At the same time, N−C bond distances in $Li_3N{=}CH_2$ and $K_3N{=}CH_2$ are extremely short (1.26−1.27 Å): the carbon atom of the CH_2 group of the former compound carries a small negative Mulliken charge (−0.15), whereas the calculated charge of the "ylidic" carbon atom in $K_3N{=}CH_2$ is even predicted to be slightly in the positive side (+0.1). The Mulliken charges on the alkali-metal atoms in both hypothetical compounds, $Li_3N{=}CH_2$ and $K_3N{=}CH_2$, are predicted to be rather small and positive (+0.15 and +0.17).

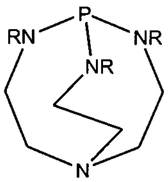
No intramolecular bond between the alkali-metal atom(s) and the carbon atom of the protonated $=CH_2$ group is predicted in protonated forms of any of the above considered ylides $Li_3P{=}CH_2$, $K_3P{=}CH_2$, $Li_3N{=}CH_2$, and $K_3N{=}CH_2$.

In the case of phosphine, ammonia, and their alkyl derivatives, the respective imines and ylides were predicted to be much stronger bases than PH_3, NH_3, and their derivatives. However, for the alkali-metal derivatives of PH_3, NH_3, and their ylides, the reversed basicity order is expected. Li_3P, K_3P, and K_3N[32] are predicted to be stronger bases than their respective ylides.

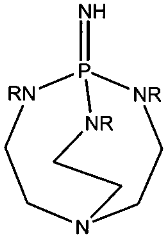
The nitrogen ylide which incorporates three NH_2 groups at the "central" nitrogen atom, $(H_2N)_3N{=}CH_2$, is found to undergo dissociation upon protonation at the CH_2 group yielding ammonia and a $[N(NH_2)(NH)CH_2]^+$ fragment.

Comparisons of Basicity of Phosphorus Imines and Ylides with Basicity of Phosphines. Simple phosphines are generally known as Brønsted bases of moderate or low strength.[1] So, the intrinsic basicity of PH_3 is higher than that of water by 23 kcal/mol but weaker than that of ammonia by 16.5 kcal/mol. However, the gas-phase basicity of trimethylphosphine is by 1.7 kcal/mol higher than that of its nitrogen analogue, Me_3N. In its turn, Et_3N is a 0.5 kcal/mol stronger base than Et_3P but equal to Ph_3P and weaker than n-Pr_3N and n-Bu_3N. The substitution of three hydrogen atoms in phosphine for (much less electronegative) lithium atoms is calculated (present work, B3LYP/6-311+G**) to lead to a real superbase Li_3P[32] (pyramidal, C_{3v} symmetry) whose predicted GB value (278.5 kcal/mol) is practically equal to that for Li_2O, and by ca. 27 kcal/mol less than that suggested for Li_3N molecule based on DFT (B3LYP/6-311++G(3df,3pd)) calculations[15] or using the results of this work (GB=305.6 kcal/mol) using a somewhat smaller 6-311+G** basis set. At the same level of DFT theory, even much stronger basicity (GB = 311.7 kcal/mol) is predicted for the potassium derivative, K_3P,[32] of phosphine. K_3P has also pyramidel C_{3V} geometry. K−P bonds are 2.92 Å. The negative charge on P is 1.61 units, and the positive charges on K are 0.536 units. K_3PH^+ has also C_{3V} symmetry, and the negative charge (−1.49) is still mostly located on phosphorus, whereas K atoms carry a large (0.846) positive charge.

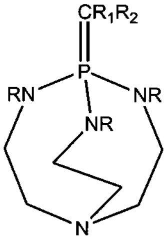
In the recent years, Verkade and co-workers have developed (see, e.g., ref 16) a series of derivatives of bicyclic phosphines, proazaphosphatranes, e.g., **5a**, which are reported to display extraordinary basic properties ($pK_a = 41.2$ in MeCN, $pK_a = 26.6$ in THF), its imides **6a** and **6b,** and ylide **7**.[33] It was suggested[16] that phosphine **5a** is in THF and MeCN of comparable base strength to t-BuP_4 phosphazene imine, a widely used commercial superbase ($pK_a = 30.4$ in DMSO,[9] $pK_a = 42.6$ in MeCN[8,9]). At the same time, **6a** was evaluated to be somewhat weaker base than **5a**. As mentioned in the introductory section, the pK_a value of **5a** was recently[17] revised and drastically downgraded by 8 powers of 10, to the basicity range of EtP_2 phosphazene base. So far, the basicity of derivatives of **7** was not estimated.



5 R=H
5a R=Me



6 R=H
6a R=Me
6b R=Ph



7 R=R$_1$=R$_2$=H
7a R=Me, R$_1$=H, R$_2$=Ph

In the present work, DFT B3LYP (6-311+G** basis) calculations of gas-phase basicity of model compounds of **5**, **6**, and **7** (R = H) were performed. The calculated intrinsic basicities of these species (244.6, 258.9, and 273.3 kcal/mol, respectively) are at odds with the suggested[16] relative solution phase basicities of these compounds: according to our present findings, the intrinsic basicity of the imine **6** exceeds the same quantity for the cyclic phosphine **5** by 14.3 kcal/mol, whereas the ylide **7** is in its turn predicted to be by 14.4 kcal/mol a stronger base than the imine base **6**, in accord with the above given discussion for the open-chain phosphorus imine and ylide bases (vide supra). Simultaneously, **5** is a much stronger base than $(H_2N)_3P$ (218.1 kcal/mol), $(Me_2N)_3P$ (230.9 kcal/mol), or Me_3P (219.3 kcal/mol) and a stronger base than $(H_2N)_3P{=}NH$ (241.1 kcal/mol) but weaker than $(H_2N)_3P{=}N{-}P(NH_2)_2{=}NH$, Li_3P, K_3P (vide supra), and higher phosphorus ylides (with $n \geq 2$), whose intrinsic basicity is expected to reach (at $n > 7$) 300 kcal/mol. At the same time, **6** and **7** are calculated to be already comparable to or stronger bases than NH_2-substituted P_1 ylide $(H_2N)_3P{=}CH_2$ (256.8 kcal/mol) or its C-methylated derivative $(H_2N)_3P{=}CMe_2$ (264.3 kcal/mol).

As a matter of fact, the strained polycycles **5**, **6**, and **7** as representatives of superbases which contain only one phosphorus atom are predicted to be significantly stronger bases than the respective open-chain derivatives of phosphines, phosphorus imines, and phosphorus ylides which also contain only one phosphorus atom. Especially impressive is the calculated basicity of **7** which is comparable to that of Li_3P and Li_2O. However, as already shown in the present discussion, various model

TABLE 7: Effect of the Replacement of the ─N═ Bridge for the ─CH═ Bridge in Phosphorus Imines and Phosphorus Ylides ($X^1 = NH_2$ and $X^2 = H$)

	═NH bases, bridge						═CH_2 bases, bridge					
	DFT/B3LYP/6-311+G**[c]		3-21G*[d]		PM3[e]		DFT/B3LYP/6-311+G**[c]		3-21G*[d]		PM3[e]	
n[a]	─N═	─CH═	─N═	─CH═	─N═	─CH═	─N═	─CH═	─N═	─CH═	─N═	─CH═
2	265.0	253.6	300.6	299.0	255.0	256.0	275.7	273.9	312.6	312.8	268.8	271.0
3[b]			316.0	316.9	269.7	276.8			331.8	339.0	288.4	290.0
3[f]									326.3	327.6	280.3	285.9
4[b]			321.0	323.6	280.0	287.8			345.1		296.5	282.4

[a] *n* is the number of phosphorus atoms. [b] The ═NH or ═CH_2 group is at the second phosphorus atom. [c] Δ*G* values (kcal/mol). [d] Protonation energies (kcal/mol). [e] Protonation enthalpies (kcal/mol). [f] The ═NH is at the terminal phosphorus atom.

TABLE 8: Effect of Consecutive Substitution of NH_2 Group by ─N═PH_3 Fragments in the $P(NH_2)_3$ Molecule[a]

	consecutive substituent NH_2	
	B3LYP/6-311+G**	
base	Δ*G*	*D*
$P(NH_2)_3$	218.1	0
$(H_2N)_2PN{=}PH_3$	234.3	16.2
$(H_2N)P(N{=}PH_3)_2$	245.8	27.7
$P(N{=}PH_3)_3$	258.3	40.2

[a] All values in kcal/mol.

iminophosphoranes and phosphoranes which contain several phosphorus atoms are predicted to be stronger bases than **5**, **6**, or even **7** in the gas phase.

The comparison of the intrinsic basicity of phosphines $X_nP[{-}N{=}PH_3]_{3-n}$ or their higher homologues, e.g., H_nP-$[({-}N{=}PH_2)_m{-}N]_{3-n}$ or $X_nP[({-}N{=}P(X_2)_{2-})_m]_{3-n}$, where X = H, NH_2, etc., with the basicity of the phosphorus imines or ylides of the same number of P atoms and carrying the same substituents X (H, NH_2, or CH_3) is interesting.

The results of DFT/B3LYP 6-311+G** level calculations of GB values of consecutive introduction of ─N═PH_3 substituents into $P(NH_2)_3$ instead of NH_2 groups are given in Tables 5 and 8.

The substitution of only one ─N═$P(NH_2)_3$ substituent into $(H_2N)_3P$ will increase the intrinsic basicity of the latter by 27.5 kcal/mol, almost to the level of Verkade's phosphatrane **5** (R = H), whereas the consecutive replacement of the amino groups of $(H_2N)_3P$ by ─N═PH_3 groups will increase the deprotonation energy by respectively 16.2, 11.5, and 12.5 kcal/mol to 258.3 kcal/mol.

Intrinsic Basicity of Imines and Ylides of Some Elements Other Than P, N, and C. Using DFT approach at the B3LYP/6-311+G** level, the dependence of the Gibbs free energy of protonation of imines and ylides of elements other than P, N, and C, e.g., oxygen, sulfur, and chlorine, on the nature of the central atom and the nature of the substituent was studied.

The substitution of an sp^2 carbon atom for a less electronegative silicon atom is expected to increase the basicity of the resulting species. This is indeed so. Silaguanidine, the molecule extensively studied by G. Frenking et al.,[27] is by 6.6 kcal/mol more basic than guanidine. Similarly, in the case of ylides, $Me_2Si{=}CH_2$ and $(H_2N)_2Si{=}CH_2$ are respectively by 35.4 and 7 kcal/mol stronger bases than their carbon analogues, whereas the calculated basicity of $(H_2N)_2Si{=}CH_2$ is comparable with that of $H_3P{=}CH_2$.

Tetraamino-substituted S(VI) imine $(H_2N)_4S{=}NH$ is expected to be by 6.2 kcal/mol a weaker base than $(H_2N)_3P{=}NH$, whereas the latter is expected to be by 10.5 kcal/mol stronger of its carbon analogue, guanidine. Pentaaminochloro(VII)imine is also expected to be weaker base than its phosphorus counterpart, $(H_2N)_3P{=}NH$, by 4.0 kcal/mol. The imines $H_2O{=}NH$ (unstable tautomer of hydroxylamine) and $H_2S{=}NH$ (tautomeric form of $HSNH_2$) are roughly of equal strength around 221 kcal/mol which is comparable to the predicted GB value for the respective phosphorus derivative, $H_3P{=}NH$ (GB = 223.4 kcal/mol).

Those trends probably reflect the basicity weakening effect of the progressive increase of the electronegativity of the "central" atom in the row $P < C \approx S < Cl$ which overpowers the stabilizing effect of the increase of the number of electron-donating amino groups of the protonated forms of the respective bases.

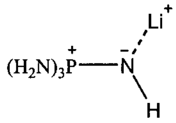
For ═CH_2 bases, similar trends hold in the row of $(NH_2)_2$-$C{=}CH_2$, $(NH_2)_3P{=}CH_2$, $(NH_2)_4S{=}CH_2$, and $(NH_2)_5Cl{=}CH_2$. The basicity is expected to increase by 19.4 kcal/mol while going from $(NH_2)_2C{=}CH_2$ to $(NH_2)_3P{=}CH_2$. Further transfer from the latter to the sulfur derivative $(NH_2)_4S{=}CH_2$ is predicted to be accompanied by a 4.9 kcal/mol drop in basicity (GB = 251.9 kcal/mol), whereas $(NH_2)_5Cl{=}CH_2$ is expected to be even weaker than its sulfur analogue by 4.4 kcal/mol. Somewhat surprisingly, the unsubstituted $H_5Cl{=}CH_2$ is calculated to be by 2.8 kcal/mol a stronger base than $(H_2N)_5Cl{=}CH_2$.

Ylides $H_2O{=}CH_2$ (high energy tautomer of MeOH; O─C bond distance in the neutral form is calculated to be 1.86 and 1.52 Å in the protonated form) and $H_2S{=}CH_2$ (tautomeric form of MeSH) are calculated to have also rather significant basicities (253.5 and 243.4 kcal/mol, respectively), which compare favorably with simple ylides of all other mentioned elements except nitrogen ($H_3N{=}CH_2$, GB = 270.7 kcal/mol, see also ref 12).

Lithium Cation Basicity of Phosphorus Imines and Ylides. On the recently published[34] gas-phase lithium cation basicity (LCB) scale of various neutral bases, the highest LCB values (up to 47.5 kcal/mol for $(C_6H_5)_3PO$ and $(Me_2N)_3PO$) belong to different phosphine oxides. The replacement of sp^2 (═O) or sp^3 (─O─) oxygen atom as basicity center toward proton for sp^2 (e.g., ═NH) or sp^3 (e.g., >N─) nitrogen atom is known[1] to lead to a very significant increase of basicity of the respective species. So, the change in $MeCONH_2$ of double-bonded ═O atom for ═NH group increases the gas-phase basicity by 30 kcal/mol. The same change in acetone molecule results in basicity increase by 36.3 kcal/mol.

Therefore, keeping in mind similar trends in changing GB and LCB[34] and experimental findings regarding the strong complex formation of Li cation with t-BuP_4 superbase,[35] one can expect that the LCB of phosphorus imines or its model compounds considered in this work would also exceed that of their oxygen analogues by a wide margin.

Indeed, the present calculations using the DFT B3LYP at 6-311+G** level show (see Table 1, footnote a, and Table 3, footnote a) that the LCB of $(H_2N)_3P{=}NH$ is expected to be as high as 59.4 kcal/mol, exceeding by ca. 12 kcal/mol the respective value for HMPA.[34] Most probably such a high LCB value evidences about strong electrostatic stabilization of the adduct by the interaction of the highly localized opposite charges on N and Li^+.



However, in contrast to phosphorus imines, the LCB basicity of the similar model compound of phosphorus ylides, $(H_2N)_3P{=}CH_2$, is calculated to be lower, at 48.7 kcal/mol, nearly equal to that of HMPA which does not correspond to the above found basicity order of those two compounds.

Our present calculations at the same level of theory show that qualitatively much higher LCB values could still be predicted for the complex formation of such inorganic superbases as Li_2O (the calculated LCB = 80.9 kcal/mol[36]), Li_3N (LCB_{calc} = 85.7 kcal/mol[37]), and K_3N (LCB_{calc} = 107.5 kcal/mol[38]). Those small inorganic molecules are characterized by extremely poor delocalization of atomic charges. So, in the neutral form of the latter superbase, the Mulliken population analysis indicates that for the N atom the negative charge is 1.83 units (+0.61 units on K atoms). For the Li^+ complex of K_3N, the expected charge separation (−1.96 on N, 0.84 on K, and 0.43 units on Li atom) is even more pronounced.

Feasibility of Gas-Phase Proton-Transfer Equilibria between a Brønsted Superbase and Superacid. The idea of a spontaneous gas-phase proton transfer between a Brønsted superacid and superbase was put forward some time ago. Several ways for realization of this idea have been suggested.[15,39] Keeping in mind the present findings that the basicity of some ylides and possibly also phosphazene imines can reach values around or beyond 300 kcal/mol and recent studies of the acidity of neutral Brønsted superacids, it is evident that a wide overlapping area exists on the unified basicity scale of neutral superbases and weak anionic bases and conjugate bases of strong or superstrong Brønsted acids.[39,40] Therefore, the spontaneous gas-phase proton transfer between neutral organic superbases, e.g., P_4 or P_5 phosphazenes and phosphorus or nitrogen ylides, and strong Brønsted acids, e.g., $HClO_4$, HBF_4, $HSbF_6$, etc., is thermodynamically achievable,[39,41] especially if one takes into account the possibility of extra stabilization from the formation of gas-phase “intimate” ion pair by electrostatic charge−charge interaction of the charges of the opposite sign.

Conclusions

The density functional theory (B3LYP/6-311+G**), ab initio (HF/3-21G*), and semiempirical (PM3) study of the intrinsic basicities and protonation energies of phosphorus imine (iminophosphoranes), phosphazene ylide, and phosphine superbases has been performed. The study shows that the representatives of the first two classes of the above-mentioned organic superbases can reach the basicity level of the strongest inorganic superbases such as alkali-metal hydroxides, hydrides, and oxides, and losing only to the hypothetical K_3N molecule whose intrinsic basicity is predicted to exceed 340 kcal/mol. The strongest organic phosphazene imine superbases are predicted to reach the gas-phase basicity level of 300 kcal/mol (at the chain length $n \geq 7-10$), whereas the strongest phosphorus ylide superbases are estimated to have (at $n \geq 5-6$) gas-phase basicity around or beyond 310−320 kcal/mol. The phosphine superbases, including Verkade’s bicyclic phosphines (proazaphosphatranes), are predicted to be of strength comparable to P_2 phosphazenes or P_1 phosphorus ylides. Extremely high basicity values and easier handling make representatives of these two series of superbases preferable to inorganic superbases as possible partners for observing the spontaneous gas-phase proton transfer between neutral Brønsted superacids and bases.

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Supporting Information Available: B3LYP/6-311+G** energies, enthalpies, free energies, and some typical structures of neutral phosphazenes, phosphoranes, and their protonated forms. This material is available free of charges via the Internet at http://pubs.acs.org.

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