Synthesis and Reactivity of Subvalent Compounds, 8[⊥]
Aromatic Phosphenium Cations[§]

Michael K. Denk,*[a] Shilpi Gupta,[a] and Alan J. Lough[a]

Dedicated to Professor Heinrich Nöth on the occasion of his 70th birthday

The aromatic stabilization of cyclic phosphenium cations (general type $C_2N_2P^+$) was studied by experimental methods (synthesis, multinuclear NMR, single crystal X-ray crystallography) and quantum chemical calculations (ab initio methods). The structures of the 1,3,2-diazaphosphole derivatives [(tBuN–CH=CH–NtBu)P⁺]Cl⁻ (**1**), (tBuN–CH₂–CH₂–NtBu)P–Cl (**2**), [(tBuN–CH=CH–NtBu)P]⁺ PF₆⁻ (**3**) and [(tBuN–CH₂–CH₂-NtBu)]P⁺ PF₆⁻ (**4**) were examined by single crystal X-ray diffraction. The chloro phosphane [(tBuN–CH=CH–NtBu)P]⁺Cl⁻ (**1**) has an ionic P–Cl bond and contains an aromatically stabilized phosphenium cation [shortest distance P···Cl = 275.9(2) pm], while the CC-saturated compound (tBuN–CH₂–CH₂–NtBu)P–Cl (**2**) is covalent. The two chloro-phosphanes **1** and **2** differ sharply in their volatility and solubility in organic solvents. Compound **2** is soluble in hydrocarbons and sublimes readily at 90 °C/0.1 Torr but **1** is insoluble in hexanes and not volatile below 180 °C/0.1 Torr. The degree of aromatic stabilization in the phosphenium cation **1** was investigated by ab initio methods. For the model cations [RN–CH₂–CH₂–NR]P⁺ and [(RN–CH=CH–NR)P]⁺, thermochemical stabilization energies of 25.8 kcal · mol⁻¹ (R = H) and 28.1 kcal · mol⁻¹ (R = Me) were obtained from isodesmic hydrogenation reactions at the RHF/MP2/6–31G*//RHF/6–31G* level.

Introduction

The aromatic stabilization of inorganic ring systems has seen renewed interest both by synthetic chemists and theoreticians.[1] We are currently involved in a comparative study of aromatically stabilized 1,3-diazole derivatives **A** and their non-aromatic counterparts **B**. The 1,3-diazoles **A** and 1,3-diazolidines **B** seem to have an unsurpassed capability to stabilize the heteroelement E in the coordination number 2.

The first stable carbenes[2] and silylenes[3] were indeed of type **A** and it is likely that other elements will likewise be stabilized in unusually low coordination numbers in systems of type **A** and **B**. Likely candidates for a successful isolation would be heterocycles that are isoelectronic with the stable carbenes and silylenes such as anionic diazoles featuring dicoordinate boron, aluminum, and gallium and cationic diazoles with dicoordinate nitrogen, phosphorus, and arsenic. Apart from the appeal to stabilize elements in unusual valence states, these species would make useful, presumably highly reactive building blocks of carbenoid reactivity.

The comparison of the respective unsaturated species **A** with the saturated counterparts **B** allows the systematic and independent variation for aromaticity and the heteroele-ment. For some elements, the experimental comparison of **A** and **B** is already possible as these species have been described in the literature. Both stable aromatic (**A**) and non-aromatic representatives (**B**) have been described for E = C,[2] Si,[3] Ge,[4] N⁺[5] and P⁺[6] and, most recently, As⁺.[7a,11b] For the elements of the boron group, the anionic diazoles **A** and **B** would be isoelectronic to the stable carbenes and silylenes but have not been reported to our knowledge.[8]
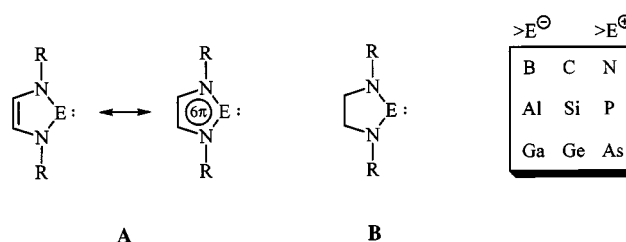

Figure 1. Aromatic 1,3-diazoles (**A**) and non-aromatic 1,3-diazolidines (**B**)

Heterocycles **A** described so far possess properties typically associated with aromatically delocalized compounds. They display unusually deshielded ring protons,[2−5] show decreased alternation in bond lengths[2−5] and exhibit reduced reactivity of **A** vs. **B**.[2−5]

For E = C,[2] Si,[3] Ge,[4] and N⁺ [5] the electronic structures of **A** and **B** were investigated by ab initio methods and photoelectron spectroscopy. These studies have demonstrated substantial delocalization of the occupied π-orbitals for **A** and a stabilization of **A** vs. **B** ranging from 13 kcal·mol⁻¹ for E = Ge[1] to as high as 38 kcal·mol⁻¹ for E = N⁺.[5] A summary of the different criteria used to

evaluate delocalization and aromaticity is available for the carbenes and silylenes. [9] Most recently, a core electron spectroscopy study by Hitchcock's group has demonstrated that the π*-orbitals of the aromatic silylenes are delocalized as well. [3e]

We have previously studied the synthesis, structure, and bonding of a series of isostructural stable carbenes, [2c] silylenes [3] and germylenes, [4] and now report on the synthesis, structure, and aromatic stabilization of the isostructural phosphenium cations **A** and **B** (R = *t*Bu in all cases). [10]

1b   **1**   **3**   **3'**

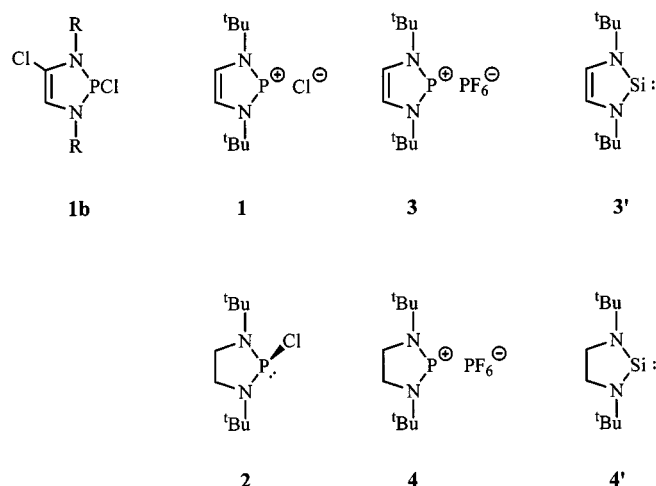

2   **4**   **4'**

Figure 2. Aromatic and non aromatic phosphenium cations and chlorophosphanes and isoelectronic stable silylenes

The compounds investigated were the chlorophosphanes [L′P]$^+$Cl$^-$ (**1**), LP−Cl (**2**), and the stable phosphenium salts [L′P]$^+$PF$_6^-$ (**3**), [LP]$^+$PF$_6^-$ (**4**), [L′P]$^+$GaCl$_4^-$ (**5**), and [LP]$^+$GaCl$_4^-$ (**6**). Our study was triggered by the remarkably different physical properties of **1** and **2**: the chlorophosphane **2** is soluble in benzene and hexanes but **1** is insoluble in hexanes and only sparingly soluble in benzene. [11] Compound **2** is quite volatile and sublimes readily at 80 °C/0.1 Torr while **1** is not volatile under these conditions. This different behavior led us to conclude that **1** is an ionic compound composed of a phosphenium cation and a chloride counterion while **2** is a covalent compound (Figure 2). [11] The crucial role of aromatic delocalization for the stabilization of **1** in its ionic form is obvious.

The related compound **1b** had previously been obtained by a special method namely in a one step synthesis from PCl$_3$ and the corresponding diazadiene R−N=CH−CH=N−R (R = *cyclo*-hexyl). [6b] While the authors noticed the long P−Cl bond length of 241.6(2) pm, they fell short of describing the compound as ionic or of relating the elongated P−Cl bond to the aromatic stabilization of the corresponding phosphenium cation. Instead, the elongation was attributed to electron donation from the two nitrogen lone pairs into the P−Cl σ*-orbital. No attempt was made to compare **1b** with the corresponding CC-saturated derivative.

As our comparison of **1** and **2** shows, the postulated donation of electron density from the nitrogen lone pairs to the P−Cl σ*-orbital alone is insufficient to induce the ionicity of **2**.
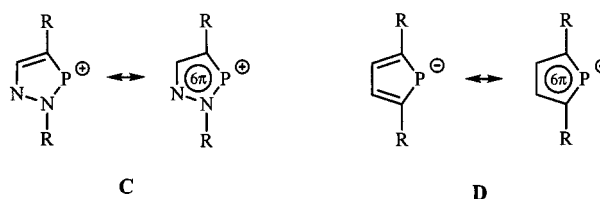

C   **D**

Figure 3. Aromatic 1,3 and 1,2-diazaphospholes

Remarkably, the isomeric 2,3-diaza-*P*-chlorophospholes **C** were recognized as ionic on the basis of their physical and spectral properties by Schmidpeter et al. [12] and the ionicity of the P−Cl bond was attributed to the formation of an aromatic phosphenium cation 6π system. [12] The anionic phospholes **D** that were recently obtained by the Mathey's group were also described as delocalized, aromatic 6π systems. [13]

Synthesis and Stability

The chlorophosphane **2** was first described by Wrackmeyer et al. who also investigated the formation of the corresponding tetrachloroaluminate from **2** and AlCl$_3$ by spectroscopic methods. [6] Compound **1** has been obtained by us via metathesis of the corresponding diazasilole with PCl$_3$ [11a] and had not been reported prior to our studies. The structures of **1** and **2** were reported by Carmalt et al. while this study was in progress. [11b]

The goal of this study was a detailed comparison of the chlorophosphanes **1** and **2** with the corresponding phosphenium cations. Our attempts to use AlCl$_3$ as chloride abstractor for **1** led to side reactions and were not pursued further. The use of GaCl$_3$ as chloride abstractor often gives cleaner reactions; [14] the tetrachlorogallates [(*t*BuN−CH=CH−N*t*Bu)P]$^+$GaCl$_4^-$ (**5**) [11a] and [(*t*BuN−CH$_2$−CH$_2$−N*t*Bu)]P$^+$GaCl$_4^-$ (**6**) [11a] were obtained from **1** and **2** without further complications. However, extensive disordering in the cation and anion sublattices precluded the determination of accurate structural data by single crystal X-ray diffraction and led us to search for new counterions. Accurate structural data were finally obtained for the hexafluorophosphates **3** and **4**. The hexafluorophosphates are easily obtained from **1** and **2** by metathesis with AgPF$_6$ in CH$_2$Cl$_2$ as colorless crystalline solids in quantitative yield.

The PF$_6$ and GaCl$_4$ salts **3**−**6** are quite soluble in dichloromethane and are easily purified by precipitation (layering) of the crude reaction solutions with hexanes. The salts **3**−**6** can be stored indefinitely under exclusion of air and moisture but the stability of the salts in solution depends critically on the nature of the counterion and the solvent. The PF$_6$ anion in the salts **3** and **4** slowly reacts with glass to form PO$_2$F$_2^-$ (and SiF$_4$) unless moisture is rigorously excluded. The reaction is easily detected by the presence of the characteristic triplet of PO$_2$F$_2^-$ (δ^{31}P = −14.7, ^1J(P,F) = 976 Hz). [15] Remarkably, the phosphenium cation is unaffected by this decomposition process. The reaction of PF$_6^-$ with glass is catalyzed by water as was

recently shown by Manzano and Otero.[15] In CDCl$_3$ solution, **3** is stable indefinitely but **4** decomposes rapidly. This difference nicely illustrates the higher reactivity (lack of aromatic stabilization) of **4**. Both phosphenium cations are significantly stabilized by the counterion GaCl$_4^-$: **5** and **6** are stable indefinitely in CD$_2$Cl$_2$ and CDCl$_3$.

Structure and Bonding

The assumption that **1** is a purely ionic compound implies a nonbonding P−Cl distance and the presence of a phosphenium cation [(tBuN−CH=CH−NtBu)P]$^+$ in the crystal lattice. To justify this assumption, a detailed comparison of the chlorophosphanes **1** and **2** with each other and also with the corresponding phosphenium cations was necessary. The structure of **1** and, for comparison, the structures of **2**−**4** were determined by single crystal X-ray crystallography.[16]

While this study was in progress, the structures of **1** and **2** were reported by Carmalt et al.[11b] For **2**, our metrical parameters differ significantly form the values reported by Carmalt et al. (see below). This is especially obvious for the P−Cl bond distance: 231.36(7) pm in this study vs. Carmalt's value of 242.5(4) pm.[11b] The value of 143(1) pm reported by Carmalt for the C−C single bond in **2** is likewise too short and results probably from an unrecognized disorder of the (nonplanar) C$_2$N$_2$P ring. The superposition of two envelope structures can present itself as structure with planar C$_2$N$_2$E geometry and artificially shortened C−C bond length resulting from projections of the true bond distances. This type of disorder is easily recognized by unusually large thermal ellipsoids for the two carbon atoms and has been described previously by us for the isoelectronic germylene.[4] The value of 150.8(3) pm that we find for the C−C distance in **2** includes a modeling of disorder of the C$_2$-bridge and is also in much better agreement with the ab initio structures (Table 4). Accordingly, the values of our single crystal X-ray diffraction study will be used for the remainder of this study. The P−Cl distance in **1** [275.9(2) pm] is substantially longer than in **2** [231.36(7) pm]. Both P−Cl distances are shorter than the sum of the van-der-Waals radii[18] of phosphorus (190 pm) and chlorine (181 pm). With P−Cl bond lengths of ≈ 210 pm being typical for the fragment N$_2$P−Cl[19], even the P−Cl bond in **2** [231.36(7) pm] must be considered as unusually elongated. A comparison of the structures of **1** and **2** with the respective genuine phosphenium (type **A** and **B**) was clearly desirable and the structures of the PF$_6$ salts **3** and **4** were studied to this end.

In the hexafluorophosphates **3** and **4**, the closest distance between the phosphorus in the phosphenium cation and the fluorine atom of the counterion is nonbonding (322 pm for **3**, 323 pm for **4**). The values are nearly identical to the sum of van-der-Waals radii for phosphorus (190 pm)[18] and fluorine (135 pm)[18] and confirm that **3** and **4** are ionic compounds. Further proof that **3** and **4** do indeed contain phosphenium cations that are unperturbed by the counterion is
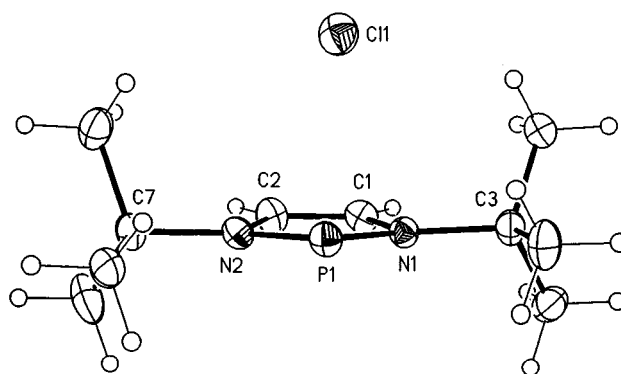

Figure 4. Molecular structure of (tBuN−CH=CH−NtBu)P$^+$Cl$^-$ **1** (0.5 C$_6$H$_6$), ORTEP view thermal ellipsoids are at the 50% probability level; selected bond lengths [pm] and bond angles [°] as follows: P(1)−N(1) 166.2(2), P(1)−N(2) 166.0(2), N(1)−C(1) 137.9(3), C(1)−C(2) 134.7(3), N(1)−C(3) 150.8(3), N(1)−P(1)−N(2) 90.41(10), P(1)−N(1)−C(1) 113.3(2), P(1)−N(1)−C(3) 123.8(2), N(1)−C(1)−C(2) 111.4(2), C(1)−N(1)−C(3) 123.8(2). Planar C$_2$N$_2$P-ring, closest P···Cl distance 275.9(2) pm.
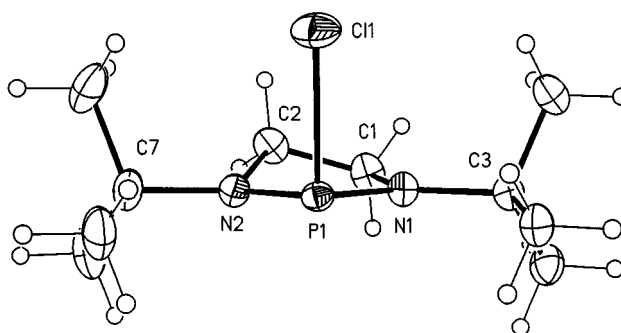
Figure 5. Molecular structure of (tBuN−CH$_2$−CH$_2$−NtBu)P−Cl (**2**), ORTEP view, thermal ellipsoids are at the 50% probability level; selected bond lengths [pm] and bond angles [°] as follows: P(1)−Cl 231.36(7), P(1)−N(1) 165.2(2), P(1)−N(2) 165.6(2), N(1)−C(1) 147.1(3), C(1)−C(2) 150.8(3), N(1)−C(3) 148.8(3), N(1)−P(1)−N(2) 92.41(8), P(1)−N(1)−C(1) 114.77(13), P(1)−N(1)−C(3) 125.20(13), C(3)−N(1)−C(1) 119.9(2), C(2)−C(1)−N(1) 105.9(2). Puckered C$_2$N$_2$P-ring.

the excellent agreement between their molecular structures and those calculated (6−31G* level) for the free phosphenium cations (compare Tables 4 and 5).

The experimental structures of **3** and **4** can now be used as a yardstick to measure the phosphenium cation character of **1** and **2**. The structures of the diazaphosphole rings in **1** and **3** are practically identical. This confirm that **1** is indeed a phosphenium chloride.

The structures of **2** and **4** on the other hand show distinct differences: The P−N bond lengths are significantly shorter in **4** [161.3(2) and 161.9(2) pm] than in **2** [165.2(2) pm and 165.6(2) pm] and the N−P−N angle in **4** [96.29(11)°] is larger than in **2** [92.41(8)°]. A more detailed comparison of other structural parameters reveals that the P−N bond distance is the most sensitive structural probe to measure the phosphenium cation character in **4**.

The P−N bond length in the aromatic **3** [166.1(2) pm] is significantly longer than in **4** [161.9(2) pm]. This somewhat counterintuitive result supports the description of **3** as delocalized system: the isolated allylic N$_2$P fragment (in **4**)
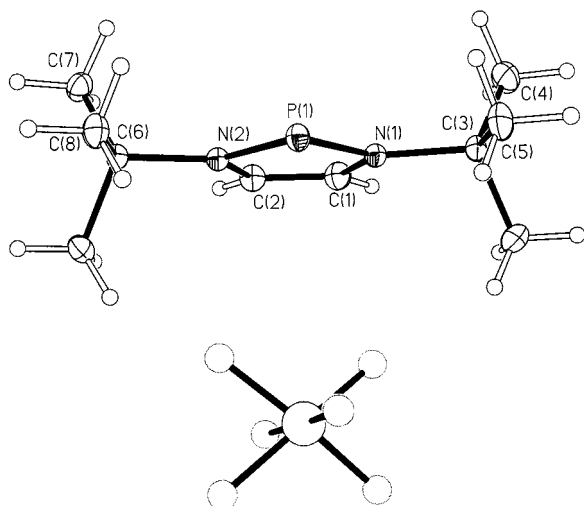
Figure 6. Molecular structure of [(*t*BuN−CH=CH−N*t*Bu)P]+·PF$_6^-$ (**3**), ORTEP view, thermal ellipsoids are at the 50% probability level; selected bond lengths [pm] and bond angles [°] as follows: P(1)−N(1) 166.1(2), P(1)−N(2) 166.2(3), N(1)−C(1) 137.6(3), C(1)−C(2) 134.1(4), N(1)−C(3) 141.2(3), N(1)−P(1)−N(2) 90.71(11), C(1)−N(1)−P(1) 112.7(2), C(2)−C(1)−N(1) 111.6(2). Planar C$_2$N$_2$P-ring, closest distance P(1)···F = 322 pm.
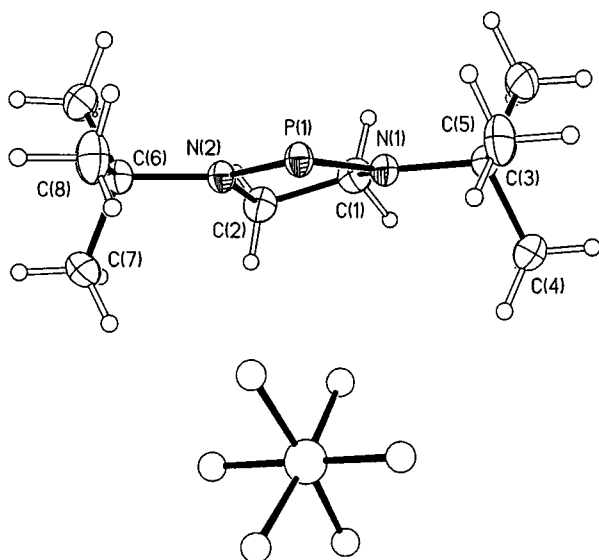
Figure 7. Molecular structure of [(*t*BuN−CH$_2$−CH$_2$−N*t*Bu)P]+PF$_6^-$ (**4**), ORTEP view, thermal ellipsoids are at the 50% probability level; selected bond lengths [pm] and bond angles [°] as follows: P(1)−N(1) 161.3(2), P(1)−N(2) 161.9(2), N(1)−C(1) 148.2(5), C(1)−C(2) 154.4(7), N(1)−C(3) 150.0(3), N(1)−P(1)−N(2) 96.29(11), C(1)−N(1)−P(1) 113.7(2), C(2)−C(1)−N(1) 105.1(4). Puckered C$_2$N$_2$P-ring, closest distance P(1)···F = 323 pm.

should experience increased delocalization and accordingly elongation of the P−N bond upon delocalization (in **3**). The nature of the phenomenon is perhaps best understood in an analogy pointed out by Sauers. [20] The C−C bond length in the cyclopentadienyl anion (141 pm) is longer than in the allyl anion (139 pm). The presence and magnitude of the effect is further evidence for a strong π-delocalization in **3**.

Silylenes R$_2$Si: are isoelectronic to phosphenium cations R$_2$P+ and a comparison of **3** and **4** with the isostructural

Table 1. Experimental bond lengths [pm] and bond angles [°] of 1,3-diazaphospholes **1**−**4** (R = *t*Bu)

	[L′P]+Cl− (1)	[L′P]+PF$_6^-$ (3)	LP−Cl (2)	[LP]+PF$_6^-$ (4)
N−P	166.0(2)	166.1(2)	165.2(2)	161.3(2)
N−P	166.2(2)	165.6(2)	165.2(2)	161.9(2)
N−C	137.9(3)	137.6(3)	147.1(3)	148.2(5)
N−C	138.9(3)	137.7(3)	147.8(2)	148.1(5)
C−C	134.7(3)	134.1(4)	150.8(3)	154.4(7)
N−P−N	90.41(10)	90.71(11)	92.41(8)	96.29(11)
N−C−C	111.4(2)	111.6(2)	105.9(2)	105.1(4)
R−N−C	122.1(2)	123.3(2)	119.9(2)	120.6(2)
P−N−C	113.3(2)	112.7(2)	114.77(13)	113.7(2)
P−N−R	123.8(2)	124.0(2)	125.20(13)	125.2(2)
Σ(N)[a]	359.2	360.0	359.9	359.5

[a] Sum of nitrogen bond angles.

stable silylenes should reveal the relative extent of aromatic stabilization in the silylenes and phosphenium cations. Table 2 compares bond distances and bond angles of the phosphenium hexafluorophosphates **3** and **4** with those of the isostructural silylenes **3′** and **4′**. The P−N distances in the phosphenium cations are ca. 4 pm shorter than one would extrapolate from the Si−N distances of the silylenes and the covalent radii of Silicon and Phosphorus. [18] This is in agreement with stronger π-bonding in the N$_2$P+−allyl system compared with the N$_2$Si−allyl system. With the exception of the element-nitrogen bond distance, the geometries of **4** and **4′** are nearly identical.

Table 2. Experimental bond lengths [pm] and bond angles [°] of isoelectronic silylenes and phosphenium cations

	[L′P]+ (3)	L′Si: (3′)	[L′P]+ PF$_6^-$ (4)	LSi: (4′)
N−E	166.1(2)	175.3(5)	161.3(2)	171.9(3)
N−C	137.6(3)	140.0(9)	148.2(5)	148.9(6)
C−C	134.1(4)	134.7(21)	154.4(7)	152.1(14)
N−E−N	90.71(11)	90.5(10)	96.29(11)	92.0(2)
N−C−C	111.6(2)	114.1(5)	105.1(4)	106.2(7)
R−N−C	123.3(2)	120.4(22)	120.6(2)	116.4(3)
E−N−C	112.7(2)	110.5(11)	113.7(2)	113.2(2)
E−N−R	124.0(2)	128.8(13)	125.2(2)	129.7(2)
Σ(N)[a]	360.0	359.7	359.5	359.3

[a] Sum of nitrogen bond angles.

The relative extent of aromatic delocalization in the two aromatic species **3** and **3′** should be reflected by the difference between formal single bonds (C−N) and formal double bonds (C=C). The C−C double bond length of the silylene **3′** [134.7(21) pm] and the phosphenium cation **3** [134.1(4) pm] are nearly identical. The C−N bond length in **3** is shortened (−2.4 pm) vs. **3′**. This shortening of a formal C−N single bond, although not dramatic, is consistent with the conclusion that phosphenium cations of type **A** possess stronger aromatic delocalization than the isoelectronic silylenes. This is also in agreement with the chemical shifts of the respective ring protons and the results of ab initio calculations (see below).

Spectroscopy

NMR investigations of **1**−**6** were concerned with ring current effects[22] and the question to what extent the phosphenium cation character of **1** and **2** is reflected by the respective ^{31}P-NMR shifts. The hexafluorophosphates **3** and **4** with a fully developed phosphenium cation were used as ionic reference compounds. The phosphenium salts **1**, **3**, and **4** show the deshielded ^{31}P-NMR resonances of phosphenium cations but appear electron rich if compared with other phosphenium cations. [21] This documents the excellent dative stabilization of **1**, **3**, and **4**. The chemical shifts vary strongly with the solvent and to a lesser degree with concentration. All measurements were therefore standardized by measuring 1 M solutions at room temperature. This standardization is essential to reveal how the solvent and the counterion influence the ^{31}P-chemical shifts.

For **1**, polar solvents lead to strong deshielding of the ^{31}P signal. In CD$_2$Cl$_2$ and CDCl$_3$, the chemical shift of the phosphorus atom approaches the value found for the fully developed phosphenium cation in **3**. We interpret this solvatochromic behavior as a result of a solvent dependent polarization of the P···Cl contact in **1**. In the case of **1**, this polarization leads to a gradual increase of aromatic delocalization that can be monitored by ^{1}H NMR (deshielding of the ring protons by the ring current).[22] The extent of aromatic delocalization in **1** can thus be fine-tuned by using solvent mixtures. For example, the chemical shift δ^{1}H of the ring protons in **1** can be varied freely between 6.38 and 7.32 by using different mixtures of C$_6$D$_6$ and CDCl$_3$.

In CDCl$_3$, the chemical shift of the ring protons in **1** (δ = 7.32) approaches the value of the phosphenium salt **3** (δ = 7.66). This is good evidence that the P−Cl bond of **1** is dissociated in CDCl$_3$. Fully as expected, the most polar solvent used in this study (CDCl$_3$) leads to the most deshielded ^{31}P-NMR shifts for **1**−**6**. However, the salt [L′P]$^+$PF$_6$$^-$ (**3**) does not follow this trend. We tentatively attribute this deviation to the onset of a covalent interaction between the chlorine lone pair of chloroform and the phosphorus atom in **3**.

The chemical shifts ^{31}P and ^{1}H also depend on the nature of the counterion. This suggests that even the electronically highly stabilized phosphenium cations investigated in this study interact with the "non coordinating"[23] counterions GaCl$_4$$^-$ and PF$_6$$^-$.

The non-aromatic series of compounds (**2**, **4**, and **6**) displays the same type of solvatochromic behavior as the aromatic series **1**, **3**, and **5**, but the solvent induced shift variation is smaller.

The outlined solvatochromic behavior is presumably indicative for the tendency of a chlorophosphane to ionize to the corresponding phosphenium cation. Compounds like PCl$_3$ that do not give rise to well stabilized phosphenium cations do not display the same solvatochromic behavior. It seems likely, that the observed solvatochromic behavior extends to other chlorophosphanes (Do)$_2$P−Cl with π-donor substituents Do. Further studies on the subject are in progress.

A comparison of NMR data for [L′P]$^+$ and the isostructural silylene and germylene is limited by the difficulties to find a common solvent. The PF$_6$ salts **3** and **4** are insoluble in C$_6$D$_6$ while the silylenes and germylenes are decomposed instantaneously by CD$_2$Cl$_2$ and CDCl$_3$. [24] If the partially developed phosphenium cation present in **1** is used instead of the fully developed phosphenium cation present in **3**, the chemical shifts of the ring protons follow the trend of thermochemical aromaticity obtained from ab initio calculations (see below):

$$L'Si < L'Ge < L'P^+$$

The solution NMR data of compound **2** do not match the symmetry of **2** in the solid state. In the crystal, the phosphorus atom in **2** is coordinated in a pseudo-tetrahedral environment. The protons of the ethylene bridge should fall into two distinct classes (*syn* and *anti* relative to the P−Cl bond) and a AA′BB′ spin system[25] should result. In CDCl$_3$ and CD$_2$Cl$_2$, the ^{1}H-NMR spectrum of **2** shows equivalent ring protons split into a well resolved doublet by ^3J coupling to the phosphorus atom. In the less polar C$_6$D$_6$, the signal of the ring protons is broadened and the ^3J coupling to the phosphorus atoms is lost. The apparent equivalence of the ring protons results from a dynamic process that is sensitive to the polarity of the solvent. A reversible dissociation of the chlorophosphane LP−Cl (**2**) into the (planar) [LP]$^+$ and Cl$^-$ would allow the reattachment of the chloride from either sides of the planar N$_2$P$^+$ fragment. The result of this process is equivalent to an inversion at the phosphorus atom. Inversion of the phosphorus lone pair is hard to reconcile with the observed solvent effects.

Table 3. Solvatochromic behavior (δ^{31}P, δ^{1}H) of chloro phosphanes (**1**, **2**) and phosphenium cations (**3**− **6**). All shifts in ppm vs. TMS (^{1}H) or 85% H$_3$PO$_4$ (^{31}P).

Solvent	Comp.	δ^{31}P	δ^{1}H(=CH)	Compound	δ^{31}P	δ^{1}H(CH$_2$)
C$_6$D$_6$	[L′P]Cl (**1**)	146.7	6.38	LP−Cl	156.0	3.00
CD$_2$Cl$_2$	[L′P]Cl (**1**)	168.6	6.97	LP−Cl	166.8	3.37
CDCl$_3$	[L′P]Cl (**1**)	177.9	7.32	LP−Cl	166.5	3.39
CD$_2$Cl$_2$	[L′P]PF$_6$ (**3**)	203.3	8.08	[LP]PF$_6$ (**4**)	262.3	4.10
CDCl$_3$	[L′P]PF$_6$ (**3**)	189.6	7.66	[LP]PF$_6$ (**4**)	decomp.	decomp.
CD$_2$Cl$_2$	[L′P]GaCl$_4$ (**5**)	191.8	7.96	[LP]GaCl$_4$ (**6**)	274.7	4.10
CDCl$_3$	[L′P]GaCl$_4$ (**5**)	195.6	7.97	[LP]GaCl$_4$ (**6**)	279.2	4.18

Computational Studies

The relative degree of aromatic delocalization can be quantified by thermochemical cycles. As experimental values are not easily available for novel aromatic systems, computational approaches play an important role.

We have previously used *isodesmic* hydrogenation reactions to establish the relative stability of silylenes[3a] and germylenes[4] and now extend this approach to the isoelectronic phosphenium cations **3** and **4**.[29] Equations **a**–**d** involve the hydrogenation of the CC double bond and were chosen to investigate the degree of aromatic delocalization by testing the thermodynamic stabilities of the model compounds **7**–**10**. The *t*Bu substituent in **3** and **4** was replaced with R = H (model compounds **7H**–**10H**) or R = Me (**7Me**–**10Me**). The phosphonium cations $R_2PH_2^+$ (**9 H, 10 H, 9Me** and **10Me**) were chosen as non-aromatic reference compounds (disrupted π-delocalization). The specific combination of basis set, correlation method and isodesmic reactions used in this study is identical to the one we used to evaluate the aromatic stabilization of germylenes and silylenes. This allows a direct comparison of the calculated aromatic stabilization energies. Compounds **A** and **B** usually require bulky alkyl- or aryl substituents to be stable enough for isolation. To save computation time, these substituents are usually replaced with hydrogen in ab initio studies. We

were interested to see how legitimate the replacement of alkyl substituents with hydrogen really is and thus have included the methyl compounds **7Me**–**10Me** in this study. While this study was in progress, the model compounds **7H** and **8H** were investigated by Sauers with a different basis set and a different set of isodesmic reactions.[20]

Aromatic stabilization energies (ASEs) for **7H** and **7Me** were obtained from the difference of the hydrogenation reactions **a** and **b** (|**a** − **b**| = ASE of **7H**) and **c** and **d** (|**c** − **d**| = ASE of **7Me**). It should be pointed out that an alternative system of isodesmic hydrogenation reactions (**e**–**h**) can be constructed from the oxidative addition of hydrogen to the phosphorus atom of the phosphenium cations **7** and **8** to give **9** and **10** respectively (Figure 8). Although the reaction energies for the equations **e**–**f** are different from those of the equations **a**–**d**, the aromatic stabilization energies obtained from both sets of equations are mathematically equivalent.[29b]

The results show a significant electronic stabilization of the unsaturated phosphenium cations **7H** and **7Me**. The methyl substituted phosphenium cation **7Me** possesses a slightly higher ASE (26.40 kcal·mol⁻¹) than the hydrogen derivative **7H** (25.73 kcal·mol⁻¹), a difference that is not only small but also well within the limits of the method. The use of the hydrogen substituted model compounds is thus fully adequate for the calculation of aromatic stabili-

Table 4. Experimental (**2**, **4**) and calculated (**8**, **10**) ring geometries (C_2N_2P) [pm] and [°] for CC-saturated 1,3-diazaphospholidines. R = exocyclic substituent at nitrogen

	LP−Cl (**2**)	[LP]⁺ PF₆⁻ (**4**)	**8Me**	**8H**	**10H**	**10Me**
N−P	165.2(2)	161.3(2)	160.1	160.2	160.4	162.2
N−C	147.1(3)	148.2(5)	147.3	147.8	148.0	147.5
C−C	150.8(3)	154.4(7)	154.2	154.4	153.2	153.1
P−H	−	−	−	−	138.2	138.5
N−P−N	92.41(8)	96.29(11)	96.1	93.9	94.0	98.2
H−P−H	−	−	−	−	104.5	103.6
N−C−C	105.9(2)	105.1(4)	106.5	105.4	104.7	105.5
R−N−C	119.9(2)	120.6(2)	118.6	119.8	120.1	119.9
P−N−C	114.77(1)	113.7(2)	115.4	117.1	112.2	110.4
P−N−R	125.20(13)	125.22	126.0	122.9	124.4	126.0
Σ(N)[a]	359.9	359.5	360.0	360.0	356.7	356.3
Point-group	C_1	C_1	C_{2v}	C_2	C_2	C_2

[a] Sum of nitrogen bond angles.

Table 5. Experimental (**1**, **3**) and calculated (**7**, **9**) ring geometries [pm] and [°] for CC-unsaturated 1,3-diazaphospholes. R = exocyclic substituent at nitrogen

	[L′P]⁺Cl⁻ (**1**)	[L′P]⁺ PF₆⁻ (**3**)	**7Me**	**7H**	**9H**	**9Me**
N−P	166.0(2)	166.1(2)	164.7	164.4	163.2	162.9
N−C	137.9(3)	137.6(3)	136.5	137.0	143.0	142.7
C−C	134.7(3)	134.1(4)	134.9	134.6	131.4	131.6
P−H	−	−	−	−	138.4	138.7
N−P−N	90.41(10)	90.71(11)	90.7	88.7	94.28	96.26
H−P−H	−	−	−	−	104.28	103.1
N−C−C	111.4(2)	112.0(2)	111.4	110.4	112.1	112.9
R−N−C	122.1(2)	123.3(2)	121.9	121.3	122.4	122.7
P−N−C	113.3(2)	112.7(2)	113.3	115.3	110.7	109.9
P−N−R	123.8(2)	124.0(2)	124.8	123.4	126.8	128.3
Σ(N)[a]	359.2	360.0	360.0	360.0	360.0	360.0
Point-group	C_1	C_1	C_{2v}	C_{2v}	C_{2v}	C_2

[a] Sum of bond angles around nitrogen.

a   7H   + H$_2$ →   8H

e   7H   + H$_2$ →   9H

b   9H   + H$_2$ →   10H

f   8H   + H$_2$ →   10H

c   7Me + H$_2$ →   8Me

g   7Me + H$_2$ →   9Me

d   9Me + H$_2$ →   10Me

h   8Me + H$_2$ →   10Me
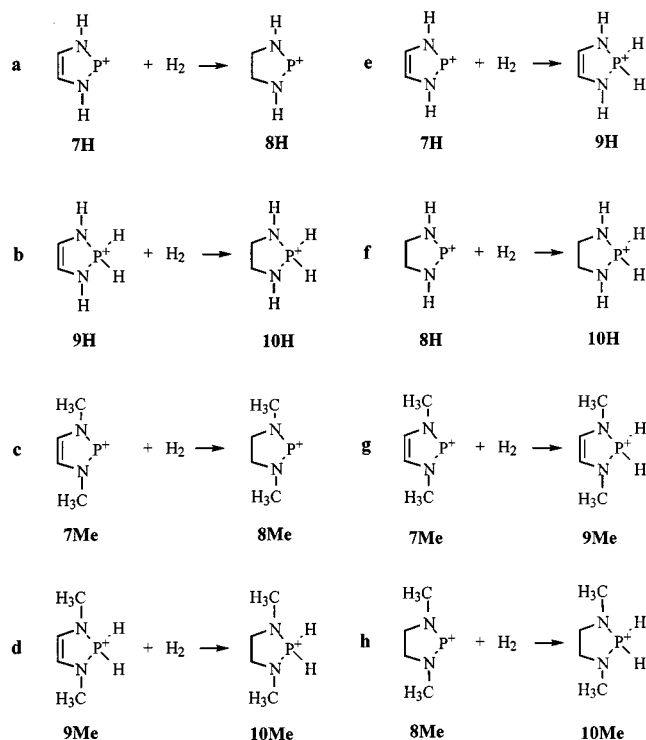
Figure 8. Isodesmic hydrogenation reactions of model compounds **7H, 9H, 7Me** and **9Me**

zation energies for the phosphenium cations and presumably for other related compounds as well.

Electron correlation at the MP2 level increases the calculated ASE values by ca. 40%. This is a good indication that the calculated ASE values represent strong differences in the degree of delocalization. Calculations at the MP4 level were restricted to the hydrogen substituted model compounds. At the MP4/6−31G*//HF/6−31G* level, a slight decrease in the ASE is observed (22.97 kcal·mol^{-1} instead of 25.73).

Table 6. Calculated reaction energies (at 0 K) for the isodesmic equations **a−h** and aromatic stabilization energies (ASE, **a−b** and **c−d**) in kcal·mol^{-1}

	6−31G*	MP2 / 6−31G*	MP4 / 6−31G*
a	−16.90	−2.57	−4.11
b	−34.92	−28.30	−27.08
c	−14.22	−0.05	−
d	−34.33	−26.49	−
e	+11.57	+32.59	+33.18
f	−6.45	+6.85	+10.21
g	+16.92	+38.05	−
h	−3.19	+11.61	−
|**a − b**|	18.02	25.73	22.97
|**c − d**|	20.11	26.44	−

The aromatic stabilization energies obtained from isodesmic equations like **a−d** and **e−h** require the construction of non-aromatic model compounds. Sauers has chosen the phosphines R$_2$P−H instead of the cationic species R$_2$PH$_2^+$ used in this study and obtained aromatic stabilization energies that are slightly smaller (24.0 kcal mol^{-1})[20] than the ones obtained from our approach.

The single crystal X-ray data obtained for **3** and **4** are in excellent agreement with the computational 6−31G* structures of the model compounds **7 H, 7Me, 8 H,** and **8Me**. Not surprisingly, the structural agreement is slightly better (especially for the N−P−N bond angles) if methyl groups are placed on the nitrogen atoms (model compounds **7Me** and **8Me**).

Conclusion

In a series of isostructural, aromatic diamino-silylenes, -germylenes, and phosphenium cations, the phosphenium cations display the highest degree of aromatic delocalization on the basis of three independent criteria: alternation of bond lengths (least), deshielding of ring protons (most), and aromatic delocalization energy (most). The experimental structures of the phosphenium cations are reproduced with excellent agreement by ab initio calculations at the 6−31G* level. The NMR shifts of the investigated phosphenium salts are strongly dependent on the polarity of the solvent.

Experimental Section

All operations were carried out with usual Schlenk techniques under Argon (99.996) or in a nitrogen filled glove box (Braun, O$_2$ < 2 ppm H$_2$O < 2 ppm). Solvents were purified by distillation from purple benzophenone/potassium solutions (hexanes, benzene) or by 30 minutes of sonication with CaH$_2$ followed by deoxygenation with three freeze-pump-thaw cycles (deuterated solvents, CH$_2$Cl$_2$). AgPF$_6$ (Aldrich) and GaCl$_3$ (Alfa) were used as received and handled in an inert gas glovebox. All NMR measurements were performed with ca. 1 M solutions in flame-sealed sample tubes at room temperature. The chemical shifts δ are reported in ppm vs. 85% H$_3$PO$_4$ (^{31}P, external) or TMS (^{1}H, ^{13}C, internal). Capillaries of 85% H$_3$PO$_4$ in D$_2$O were used as internal reference for the ^{31}P-NMR measurements. Positive shift values represent deshielding relative to the standard. The NMR samples were observed over a period of 4 months for signs of decomposition. Satisfactory elemental analysis (C,H,N) were obtained for **1−4**. Single crystals were grown by slow sublimation (**1**, **2**) or by layering of half-saturated CH$_2$Cl$_2$ solutions with hexanes (**3**, **4**). Compounds **1** and **2** were obtained as described previously.[11]

Synthesis of 3/4: To a stirred solution of 1 mmol of the chlorophosphane (234 mg, **1** or 236 mg, **2**) dissolved in 20 mL of dichloromethane was added a solution of 1 mmol of AgPF$_6$ (253 mg) dissolved in 20 mL of dichloromethane dropwise and under exclusion of light. The mixture was stirred for 1 h, decanted from the precipitate (AgCl) with a syringe, the total volume reduced to 20 mL and the remaining solution layered with 20 mL of hexanes. The hexafluorophosphates **3/4** crystallized as analytically pure, colorless crystals and were isolated by filtration through a medium size frit and washing with 10 mL of hexanes. Yields: 95−100%. The analytically pure tetrachlorogallates **5/6** were obtained in analogous fashion from **1/2** (10 mmol) by treating with GaCl$_3$ (10 mmol 10% in benzene). The solvent was evaporated, the residue dissolved in 20 mL of CH$_2$Cl$_2$ and the resulting solution layered with 20 mL of hexanes, yields 90−95%.

The salts **3−6** can be stored indefinitely under exclusion of air and moisture. Single crystals for X-ray crystallography were grown by

recrystallization from boiling benzene (**1**), slow sublimation (**2**) or by layering of CH$_2$Cl$_2$ solutions with hexanes (**3**−**6**).

Spectroscopic Data

1: ^{1}H NMR (CD$_2$Cl$_2$): δ = 1.63 [d, ^4J(P,H) = 1.8 Hz, 18 H, CH_3], 6.97 [d, ^3J(P,H) = 1.5 Hz, 2 H, CH]. − ^{13}C NMR: δ = 30.41 [d, ^3J(C,P) = 10.3 Hz, CH$_3$], 57.83 [d, ^2J(C,P) = 7.4 Hz, CMe$_3$], 121.34 [d, ^2J(C,P) = 8.8 Hz, =CH]. − ^{31}P NMR (CD$_2$Cl$_2$): δ = 168.6 (s, br). − IR (Nujol, CsI, cm^{-1}): ν̃ = 1201 s, 1079 s, 1020 m, 842 m, 790 m, 723 vs, 535 m. − **2**: ^{1}H NMR (CD$_2$Cl$_2$): δ = 1.39 [d, ^4J(P,H) = 1.8 Hz, 18 H, CH_3], 3.37 [d, ^3J(P,H) = 6.6 Hz, 4 H, CH_2]. − ^{13}C NMR (CD$_2$Cl$_2$): δ = 28.97 [d, ^3J(C,P) = 11.7 Hz, CH$_3$], 45.78 [^2J(C,P) = 10.2 Hz, CH$_2$$CH_2$], 54.10 [$^2J$(C,P) = 11 Hz, CMe$_3$]. − ^{31}P NMR (CD$_2Cl_2$): δ = 166.8 (s, br). − IR (Nujol, CsI, cm^{-1}): ν̃ = 1222 s, 1209 s, 1125 m, 1089 w, 1041 s, 983 m, 863 m, 802 m, 723 w, 677 s, 666 s. − **3**: ^{1}H NMR (CD$_2$Cl$_2$): δ = 1.78 [d, ^4J(P,H) = 1.9 Hz, 18 H, CH_3], 8.08 (s, 2 H, =CH). − ^{13}C NMR (CD$_2$Cl$_2$): δ = 31.48 [d, ^3J(C,P) = 8.8 Hz, CH$_3$], 53.59 [d, ^2J(C,P) = 27.1 Hz, CMe$_3$], 132.96 [d, ^2J(C,P) = 2.9 Hz, =CH]. − ^{31}P NMR (CD$_2$Cl$_2$): δ = 202.3 (s, br, N$_2$P$^+$), −144.6 [hept, ^1J(P,F) = 711.1 Hz, PF$_6^-$]. The phosphorus chemical shift for PF$_6^-$ is in good agreement with published values (δ = 142.1, ^1J = 717 Hz).[15] − IR (Nujol, CsI, cm^{-1}): ν̃ = 1304 m, 1261 m, 1205 w, 1192 w, 1148 m, 1075 m, 1020 m, 830 vs, 803 m, 738 w, 723 m, 558 s, 476 w. − **4**: ^{1}H NMR (CD$_2$Cl$_2$): δ = 1.58 [d, ^4J(P,H) = 2.2 Hz, 18 H, CH_3], 4.10 [d, ^3J(P,H) = 4.5 Hz, 4 H, CH_2]. − ^{13}C NMR (CD$_2$Cl$_2$): δ = 29.68 [d, ^3J(P,C) = 9.5 Hz, CH$_3$], 48.61 [d, ^2J(P,C) = 8.8 Hz, CH$_2$], 53.60 [d, ^2J(P,C) = 27.0 Hz, CMe$_3$]. − ^{31}P NMR (CD$_2$Cl$_2$): δ = +262.3 (s, br, N$_2$P$^+$), −144.6 [hept, ^1J(P,F) = 711.1 Hz, PF$_6^-$]. The phosphorus chemical shift for PF$_6^-$ is in agreement with published values (δ = 142.1, ^1J = 717 Hz).[15] − IR (Nujol, CsI, cm^{-1}): ν̃ = 1299 w, 1282 w, 1261 m, 1194 s, 1158 m, 1144 m, 1121 m, 1093 w, 1037 s, 1012 m, 986 w, 934 w, 876 m, 835 vs, 740 m, 723 s, 670 w, 558 vs.

Acknowledgments

[1] F. Bernardi, A. Bottoni, A. Venturini, *J. Mol. Struct. (Theochem)* **1988**, *163*, 173−189. − K. K. Baldridge, M. S. Gordon, *J. Am. Chem. Soc.* **1988**, *110*, 4204−4208. − A. R. Katritzy, P. Barczynski, G. Musumarra, D. Pisano, M. Szafran, *J. Am. Chem. Soc.* **1989**, *111*, 7−15. − M. N. Glukhovtsev, B. Ya. Simkin, *Organometal. Chem. USSR* **1990**, *3*, 545−554. − V. I. Minkin, M. N. Glukhovtsev, B. Ya. Simkin, *Aromaticity and Antiaromaticity*, Chapter 2, Wiley, New York **1994**. − P. v. R. Schleyer, P. K. Freeman, H. Jiao, B. Goldfuss, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 337−340; *Angew. Chem.* **1995**, *107*, 332−326. − L. Nyulászi, P. Várnai, T. Veszprémi, *J. Mol. Struct. (Theochem)* **1995**, *358*, 55−61. − P. v. R. Schleyer, H. Jiao, *Pure Appl. Chem.* **1996**, *68*, 209−218. − J. Su, X. −W. Li, R. C. Crittendon, G. H. Robinson, *J. Am. Chem. Soc.* **1997**,

119, 5471−5472. − A. Sekiguchi, M. Tsukamoto, M. Ichinohe, *Science* **1997**, *275*, 60−61.

[2] [2a] A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361−363. − [2b] G. Boche, C. Hilf, K. Harms, M. Marsch, J. C. W. Lorenz, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 487−489; *Angew. Chem.* **1995**, *107*, 509−513. − [2c] M. K. Denk, A. Thadani, K. Hatano, A. J. Lough, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2607−2609; *Angew. Chem.* **1997**, *109*, 2719−2721.

[3] [3a] M. Denk, R. Lennon, R. Hayashi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner, N. Metzler, *J. Am. Chem. Soc.* **1994**, *116*, 2691−2692. − [3b] M. Denk, R. K. Hayashi, R. West, *J. Chem. Soc., Chem. Commun.* **1994**, 33−34. − [3c] M. Denk, J. Green, N. Metzler, M. Wagner, *J. Chem. Soc., Dalton Trans.* **1994**, 2405−2410. − [3d] N. Metzler, M. Denk, *J. Chem. Soc., Chem. Commun.* **1996**, 2657−2658. − [3e] S. Urquhart, A. P. Hitchcock, J. Lehman, M. K. Denk, *Organometallics* **1998**, *17*, 2352−2360.

[4] W. A. Herrmann, M. Denk, J. Behm, W. Scherer, F.-R. Klingan, H. Bock, B. Solouki, M. Wagner, *Angew. Chem.* **1992**, *104*, 1489−1492; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1485−1488. *For a detailed discussion of the C$_2$N$_2$E disorder see:* J. Behm, Ph. D. Dissertation, Technische Universität München, **1992**.

[5] G. Boche, P. Andrews, K. Harms, M. Marsch, K. S. Rangappa, M. Schimeczek, C. Willeke, *J. Am. Chem. Soc.* **1996**, *118*, 4925−4930.

[6] [6a] B. Wrackmeyer, J. Schiller, *Z. Naturforsch.* **1992**, *47b*, 662−667. − [6b] R. B. King, P. M. Sundaram, *J. Org. Chem.* **1984**, *49*, 1784. − [6c] A. M. Kibardin, I. A. Litvinov, V. A. Naumov, Yu. T. Struchkov, T. V. Gryaznova, Yu. B. Mikhailov, A. N. Pudovnik, *Dokl. Akad. Nauk SSSR* **1994**, *312*, 623−625. − [6d] A. M. Kibardin, I. A. Litvinov, V. A. Naumov, Yu. T. Struchkov, T. V. Griaznova, J. B. Michailov, *Dokl. Akad. Nauk. SSSR* **1988**, *298*, 369−373.

[7] N. Burford, J. A. C. Clyburn, P. Losier, T. M. Parks, T. S. Cameron, J. F. Richardson, *Phosphorus, Sulfur and Silicon* **1994**, *93/94*, 301−304. − N. Burford, T. M. Parks, G. Wu, *Phosphorus, Sulfur and Silicon* **1994**, *93/94*, 397−398. − N. Burford, C. L. B. Macdonald, T. M. Parks, G. Wu, B. Borecka, W. Kwiatkowski, T. S. Cameron, *Can. J. Chem.* **1996**, *74*, 2209−2216.

[8] *The dicoordinate anion Ph$_2$B$^-$ has been suggested as a possible intermediate in the photolytic decomposition of the tetraphenylborate anion:* J. J. Eisch, K. Tamao, R. J. Wilcsek, *J. Am. Chem. Soc.* **1975**, *97*, 895−897. − J. J. Eisch, B. Shafi, M. P. Boleslawski, *Pure & Appl. Chem.* **1991**, *63*, 365−368. − *Note added in proof:* The anionic group(III) diazoles of type **A** and **B** have been investigated by ab initio methods, A. Sundermann, M. Reiher, W. W. Schoeller, *Eur. J. Inorg. Chem.* **1998**, 305−310. − For efforts directed towards the synthesis of stable dicoordinate gallium derivatives see: A. H. Cowley, D. S. Brown, A. Decken, S. Kamepalli, *J. Chem. Soc., Chem. Commun.* **1996**, 2425−2426.

[9] C. Heinemann, T. Müller, Y. Apeloig, H. Schwarz, *J. Am. Chem. Soc.* **1996**, *118*, 2023−2038. − L. Nyulászi, T. Karpati, T. Veszprémi, *J. Am. Chem. Soc.* **1994**, *116*, 7239−7242. − C. Boehme, G. Frenking, *J. Am. Chem. Soc.* **1996**, *118*, 2039−2046.

[10] *For general publications on phosphenium cations see:* I. Kawada, R. Allmann, *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 69−70; *Angew. Chem.* **1968**, *80*, 40−41. − S. Fleming, M. K. Lupton, K. Jekot, *Inorg. Chem.* **1972**, *11*, 2534−2540. − M. G. Thomas, C. W. Schultz, R. W. Parry, *Inorg. Chem.* **1977**, *16*, 994−1001. − A. H. Cowley, M. C. Cushner, J. S. Szobota, *J. Am. Chem. Soc.* **1978**, *100*, 7784−7786. − L. D. Hutchinson, E. N. Duesler, R. T. Paine, *Organometallics* **1982**, *1*, 1254−1256. − A. Cowley, R. A. Kemp, *Chem. Rev.* **1985**, *85*, 367−382. − M. Sanchez, M. −R. Mazieres, R. Bartsch, R. Wolf, J. −P. Majoral, *Phosphorus and Sulfur* **1987**, *30*, 487−490. − R. Bartsch, M. Sanchez, R. Wolf, *Phosphorus and Sulfur* **1988**, *35*, 89−92. − A. Schmidpeter, M. Thiele, *Angew. Chem.* **1991**, *103*, 333−335. − N. Burford, J. A. C. Clyburne, P. K. Bakshi, T. S. Cameron, *J. Am. Chem. Soc.* **1993**, *115*, 8829−8830. − N. Burford, P. Losier, K. Bakshi, T. S. Cameron, *J. Chem. Soc., Dalton Trans.* **1993**, 201−202. − N. Burford, P. Losier, C. Macdonald, V. Kyrimis, P. K. Bakshi, T. S. Cameron, *Inorg. Chem.* **1994**, *33*, 1434−1439. − N. Burford, P. Losier, S. V. Sereda, T. S. Cameron, G. Wu, *J. Am. Chem. Soc.* **1994**, *116*, 6474−6475. − R. W. Reed, Z. W. Xie, J. Manning, R. Mathur, R. Bau, C. A. Reed, *Phosphorus, Sulfur and Silicon and related Elements* **1994**, *93*, 485−485. −

N. Burford, J. A. C. Clyburne, P. Losier, T. M. Parks, T. S. Cameron, *Phosphorus, Sulfur and Silicon and related Elements* **1994**, *93*, 301−304. − T. Kaukorat, I. Neda, R. Schmutzler, *Coord. Chem. Rev.* **1994**, *137*, 53−107. − R. W. Reed, Z. W. Xie, C. A. Reed *Organometallics* **1995**, *14*, 5002−5004. − A. Schmidpeter in: *Comprehensive Heterocyclic Chemistry* (eds. A. Katritzky, C. Rees, E. Scriven), Vol. 4, Pergamon, **1996**, 711−818.

[11] [11a] M. K. Denk, S. Gupta, R. Ramachandran, *Tetrahedron Lett.* **1996**, *37*, 9025−9028. − [11b] C. J. Carmalt, V. Lomeli, B. G. McBurnett, A. H. Cowley, *J. Chem. Soc., Chem. Commun.* **1997**, 2095−2096. − [11c] D. Gudat, *Eur. J. Inorg. Chem.* **1998**, 1087−1094.

[12] J. Luber, A. Schmidpeter, *Angew. Chem Int. Ed. Engl.* **1976**, *15*, 111−112; *Angew. Chem.* **1976**, *88*, 91−92. − P. Friedrich, G. Huttner, J. Luber, A. Schmidpeter, *Chem. Ber.* **1978**, *111*, 1558−1563. − J. H. Weinmaier, J. Luber, A. Schmidpeter, S. Pohl, *Angew. Chem.* **1979**, *91*, 442−443; *Angew. Chem. Int. Ed.* **1979**, *18*, 412−413. − J. H. Weinmaier, G. Brunnhuber, A. Schmidpeter, *Chem. Ber.* **1980**, *113*, 2278−2290. − K. Karaghiosoff, J.-P. Majoral, A. Meriem, J. Navech, A. Schmidpeter, *Tetrahedron Lett.* **1983**, *24*, 2137−2140. − K. Karaghiosoff, W. S. Sheldrick, A. Schmidpeter, *Chem. Ber.* **1986**, *119*, 3213−3226.

[13] D. Carmichael, L. Ricard, F. Mathey, *J. Chem. Soc., Chem. Commun.* **1994**, 1167−1168. − F. Mathey, *Phosphorus Sulfur and Silicon and the related elements* **1994**, *87*, 139−148. − F. Mathey, *J. Organomet. Chem.* **1994**, 25−30. − H. J. Gosink, F. Nief, L. Ricard, F. Mathey, *Inorg. Chem.* **1995**, *34*, 1306−1307.

[14] N. Burford, J. Clyburn, personal communication, **1995**.

[15] R. Fernández-Galan, B. R. Manzano, A. Otero, M. Lanfranchi, M. A. Pelinghelli, *Inorg. Chem.* **1994**, *33*, 2309−2312.

[16] Crystal data for [L′P]$^+$Cl$^-$ (**1**): The compound crystallizes with 0.5 equivalents of benzene, C$_{10}$H$_{20}$ClN$_2$P • 0.5 C$_6$H$_6$, M = 273.75, crystal size = 0.5 × 0.4 × 0.2 monoclinic, space group $P2_1$/n, a = 11.056(2), b = 11.244(2), c = 13.512(2) Å, ß = 113.872(13)°, V = 1536.0(5) Å^3, Z = 4, $d_{calc.}$ = 1.184 g·cm^{-3}, λ(Mo-K_α) = 0.71073 Å, μ(Mo-K_α) = 0.336 mm^{-1}, $F(000)$ = 588, scan type 2θ−θ, T = 113(2) K, 2.02 < 2θ < 22.50°, total unique data 2000 (R_i = 0.039), no. of observations [(F) > 4σ(F)] 4223, R = 0.034, R_w = 0.071, maximum peak in final Fourier difference synthesis 0.232 eÅ^{-3}. − Crystal data for LPCl (**2**): C$_{10}$H$_{22}$ClN$_2$P, M = 236.72, crystal size = 0.5 × 0.4 × 0.2 orthorhombic, space group $Pbca$, a = 11.8843(8), b = 11.118(2), c = 19.899(2) Å, V = 2629.2(6) Å^3, Z = 8, $d_{calc.}$ = 1.196 g·cm^{-3}, λ(Mo-K_α) = 0.71073 Å, μ(Mo-K_α) = 0.382 mm^{-1}, $F(000)$ = 1024, scan type 2θ−θ, T = 113(2) K, 2.02 < 2θ < 22.49°, total unique data 1719 (R_i = 0.026), no. of observations [(F) > 4σ(F)] 3434, R = 0.027, R_w = 0.065, maximum peak in final Fourier difference synthesis −0.184 eÅ^{-3}. − Crystal data for [L′P]$^+$[PF$_6$]$^-$ (**3**): C$_{10}$H$_{20}$F$_6$N$_2$P$_2$, M = 344.22, crystal size = 0.35 × 0.45 × 0.35 orthorhombic, space group $Pnma$, a = 12.149(2), b = 8.3440(9), c = 15.431(3) Å, V = 1564.2(4) Å^3, Z = 4, $d_{calc.}$ = 1.462 g·cm^{-3}, λ(Mo-K_α) = 0.71073 Å, μ(Mo-K_α) = 0.331 mm^{-1}, $F(000)$ = 712, scan type 2θ−θ, T = 168(2) K, 5.28 < 2θ < 59.98°, total unique data 2422 (R_i = 0.0000%), no. of observations [(F) > 4σ(F)] 1618, R = 0.045, R_w = 0.071, maximum peak in final Fourier difference synthesis 0.535 eÅ^{-3}. − Crystal data for [LP]$^+$[PF$_6$]$^-$ (**4**): C$_{10}$H$_{22}$F$_6$N$_2$P$_2$, M = 346.24, crystal size = 0.32 × 0.27 × 0.19 orthorhombic, space group $Pnma$, a = 11.6987(11), b = 8.349(2), c = 16.1957(12) Å, V = 1581.8(4) Å^3, Z = 4, $d_{calc.}$ = 1.454 g·cm^{-3}, λ(Mo-K_α) = 0.71073 Å, μ(Mo-K_α) = 0.328 mm^{-1}, $F(000)$ = 720, scan type 2θ−θ, T = 173(2) K, 5.04 < 2θ < 60.00°, total unique data 2454 (R_i = 0.0000), no. of observations [(F) > 4σ(F)] 1656, R = 0.0495, R_w = 0.1325, maximum peak in final Fourier difference synthesis 0.513 eÅ^{-3}. Data were collected on a *Siemens P4* diffractometer. No absorption correction was applied. Lorentz and polarization corrections were applied. Systematically absent reflexions were rejected and equivalent reflexions were merged. The heavy-atom positions were determined by direct methods. Subsequent difference Fourier synthesis revealed the positions of all other non-hydrogen atoms, organic hydrogen atoms were put into idealized position. The non-hydrogen atoms were refined by the full-matrix least-squares method with the hydrogen atoms "riding" on their supporting carbon atoms. A weighting scheme (w^{-1} = σ^2(F) + 0.001·F^2) was applied and the data were corrected for the effects of anomalous dispersion and secondary extinction. Crystallographic calculations were carried out using the *Siemens SHELXS-86* program [17a] on a *Silicon Graphics Indigo2* system in the *Chemical Crystallography Laboratory, University of Wisconsin, Madison*, USA (compounds **1** and **2**) or with the SHELXTL/PC [17b] program, version 5.1, on a Pentium 133 PC in the *Chemical Crystallography Laboratory, University of Toronto*, Canada (compounds **3**−**6**).

[17] [17a] G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467−473. − [17b] *Bruker Analytial X-ray Systems*, Madison, Wisconsin, USA, **1998**.

[18] J. Emsley, *The Elements*, 2nd edition, Clarendon Press, Oxford, **1991**.

[19] e.g. 210.5(9) pm in the *trans*-1,3-(Di-*tert*-butyl)-2,4-dichlorodia-zadiphosphetidine, *cyclo*-(tBuN)$_2$(PCl)$_2$, K. W. Muir, J. F. Nixon, *J. Chem. Soc., Chem. Commun.* **1971**, 1405−1406.

[20] R. R. Sauers, *Tetrahedron* **1997**, *53*, 2357−2364.

[21] A. Schmidpeter, K. Karaghiosoff, in: *CRC Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data* (John C. Tebby, ed.), CRC Press, Boca Raton, **1991**.

[22] *For ring current theories in Nuclear Magnetic Resonance see:* C. W. Haigh, R. B. Mallion, *Prog. NMR Spectroscopy*, **1980**, *13*, 103−344.

[23] *For reviews on weakly coordinating anions see:* W. Beck, K. Sünkel, *Chem. Rev.* **1988**, *88*, 1405−1416. − T. J. Marks, *Acc. Chem. Res.* **1992**, *25*, 57. − S. H. Strauss, *Chem. Rev.* **1993**, *93*, 927−942. − D. M. van Seggen, P. K. Hurlburt, O. P. Anderson, S. H. Strauss, *Inorg. Chem.* **1995**, *34*, 3453.

[24] M. K. Denk, unpublished results.

[25] E. Lustig, E. P. Ragelis, N. Duy, J. A. Ferretti, *J. Am. Chem. Soc.* **1967**, *89*, 3953−3959, R. A. Hoffmann, S. Forsén, in: *NMR, Basic Principles and Progress* **1971**, *5*, 1−165 (Eds.: P. Diehl, E. Fluck, R. Kosfeld).

[26] Cerius2^{TM} 2.0 was developed by *Molecular Simulations Inc.* (see also http://www.msi.com).

[27] *Gaussian 94, Revision D.4*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. J. Wong, L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, *Gaussian, Inc.*, Pittsburgh, PA, **1995**. Website: http://www.gaussian.com.

[28] W. J. Hehre, C. Radom, P. v. R. Schleyer, J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, **1986**.

[29] [29a] Equilibrium geometries were calculated with *Cerius*^{2TM} [26] using *Gaussian 94*. [27] Calculations were performed without symmetry restrictions. The structures were calculated at the 6−31G* level [28] and the absence of virtual frequencies for the optimized geometries was confirmed by frequency analysis at this level. Zero-point energies were calculated at the 6−31G* level and multiplied by 0.89 to correct for anharmonicity. [28] Relative energies at 0 K were obtained by adding the corrected zero-point vibrational energies to the electronic energies. Final electronic energies were obtained by single-point calculations including electron correlation at the MP2 level in the 6−31G* basis set with the optimized RHF/6−31-G* geometries (RHF/MP2/6−31G*//RHF/6−31G*). The energies were converted to kcal·mol^{-1} using the factor 1 Hartree = 627.59 kcal·mol^{-1}. − [29b] e.g.: **a** − **b** = (**7H** + H$_2$ − **8H**) − (**9H** + H$_2$ − **10H**) = (**7H** + H$_2$ − **9H**) − (**8H** + H$_2$ − **10H**) = **e** − **f**.

[30] Crystallographic data (excluding structure factors) for the structures of **1**−**4** have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication no. CCDC−101272. Copies of the data can be obtained free of charge on applications to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: Int. Code +44 (1223) 336−033. E-mail: deposit@chemcrys.cam.ac.uk].