Stability and Electrophilicity of Phosphorus Analogues of Arduengo Carbenes—An Experimental and Computational Study

Dietrich Gudat,* Asadollah Haghverdi, Heike Hupfer, and Martin Nieger[a]

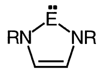
Dedicated to Professor Manfred Meisel on the occasion of his 60th birthday

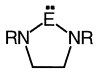
Abstract: A variety of differently substituted 1,3,2-diazaphospholenium salts and *P*-halogeno-1,3,2-diazaphospholenes (X = F, Cl, Br) were synthesized, and their molecular structures, bonding situation, and Lewis acid properties were characterized by experimental (single-crystal X-ray diffraction, NMR and IR/Raman spectroscopy, MS, conductometry, titrations with Lewis bases) and computational methods. Both experimental and computational investigations confirmed that the structure and bonding in the diazaphospholenium cations of OTf and BF_4 salts resembles that of neutral Arduengo carbenes and that the cations should not be described as genuinely aromatic. *P*-Halogenodiazaphospholenes are, in contrast to earlier assumptions, molecular species with covalent P–X bonds whose bonding situation can be expressed in terms of hyperconjugation between the six π electrons in the C_2N_2 unit and the σ*(P–X) orbital. This interaction induces a weakening of the P–X bonds, whose extent depends subtly on substituent influences and contributes fundamentally to the amazing structural similarity of ionic and covalent diazaphospholene compounds. A further consequence of this effect is the unique polarizability of the P–Cl bonds in *P*-chlorodiazaphospholenes, which is documented in a considerable spread of P–X distances and bond orders. Measurement of the stability constants for complexes of diazaphospholene compounds with Lewis bases confirmed the lower Lewis acidities and higher stabilities of diazaphospholenium ions as compared with nonconjugated phosphenium ions; this had been inferred from computed energies of isodesmotic halide-transfer reactions, and permitted also to determine equilibrium constants for P–Cl bond dissociation reactions. The results suggest, in accord with conductance measurements, that *P*-chlorodiazaphospholenes dissociate in solution only to a small extent. On the basis of these findings, the unique solvatochromatic behavior of NMR chemical shifts of these compounds was attributed to solvent-dependent P–Cl bond polarization rather than to shifts in dissociation equilibria.

Keywords: donor–acceptor systems · Lewis acids · phosphenium cations · phosphorus heterocycles · substituent effects

Introduction

The discovery of stable carbenes by Bertrand[1] and Arduengo[2] lead to a renaissance of the chemistry of subvalent compounds of Group 14 elements.[3] Among the first isolable carbenes were heterocycles of type **A** (E = C) whose six π electrons in the ring offer the possibility of aromatic stabilization. Extensive experimental[4] and theoretical studies[5] of structure and bonding in these compounds suggest that such cyclic π delocalization contributes far less to the overall stability than N → C π donation into the empty p orbital at the carbon atom.[5] Consequently, saturated cyclic (B, E = C) or acyclic diaminocarbenes (C, E = C) should also be likely candidates for successful isolation, and have meanwhile been prepared.[6] A similar bonding situation as in carbenes of type **A** prevails in homologous silylenes (E = Si)[7] and germylenes (E = Ge).[8]


A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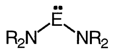
C

E = C, Si, Ge, P^+, As^+

Beside neutral compounds of type **A**–**C** with heavier Group 14 elements, ionic carbene analogues can be conceived by formal replacement of the carbon by a positively or

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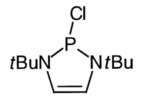
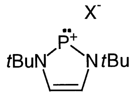
negatively charged element of an adjacent main group. Whereas anions with elements of the boron group are still hardly explored,[9] stable phosphenium (E = P$^+$) and arsenium (E = As$^+$) cations of type **B** and **C** are long known,[10,11] and their carbene analogue behavior has been verified by extensive chemical investigations.[10] Recently, the groups of Pudovik[12] and Denk[13] prepared 1,3,2-diazaphospholenium ions (**A**, E = P$^+$), which are isoelectronic and isolobal to Arduengo carbenes, and likewise nitrogen derivatives of **A**[14] have been reported. Theoretical and experimental studies[12–15] suggested that cyclic π delocalization is more pronounced in cationic than in neutral carbene analogues, and phosphenium ions of type **A** are both more stable and less electrophilic than their analogues with structures **B** and **C**.

Abstract in German: *Eine Reihe unterschiedlich substituierter 1,3,2-Diazaphospholeniumsalze und P-Halogeno-1,3,2-diazaphospholene (X = F, Cl, Br) wurde synthetisiert und hinsichtlich ihrer Molekülstrukturen, Bindungssituation und Lewis-Säure-Eigenschaften durch experimentelle (Einkristallröntgenstrukturanalyse, NMR, IR/Raman, MS, Konduktometrie, Titrationen mit Lewis-Basen) und theoretische Methoden charakterisiert. Sowohl experimentelle und theoretische Befunde legen nahe, daß die Diazaphospholeniumkationen in OTf- und BF_4-Salzen hinsichtlich Struktur und Bindungssituation enge Analogien zu neutralen Arduengo-Carbenen zeigen und nicht als genuine aromatische Systeme beschrieben werden sollten. P-Halogenodiazaphospholene sind demgegenüber, abweichend von früheren Annahmen, molekulare Systeme mit kovalenten P-X-Bindungen, deren Bindungssituation im Sinn einer Hyperkonjugation zwischen den 6 π-Elektronen der C_2N_2-Einheit und dem σ*(PX)-Orbital dargestellt werden kann. Diese Wechselwirkung führt zu einer Schwächung der P–X-Bindungen, deren Ausmaß stark von Substituenteneinflüssen abhängt, und trägt wesentlich zu der auffallenden strukturellen Ähnlichkeit zwischen ionischen und kovalenten Diazaphospholenderivaten bei. Als weitere Folge dieses Effektes resultiert eine besonders ausgeprägte Polarisierbarkeit der P–Cl-Bindungen in P-Chlor-Diazaphospholenen, die sich in einer beträchtlichen Variationsbreite von P–Cl-Abständen und Bindungsordnungen dokumentiert. Messungen der Stabilitätskonstanten der Komplexe von Diazaphospholenderivaten mit Lewis-Basen bestätigen die aus berechneten Energien isodesmotischer Halogenidübertragungsreaktionen postulierten geringeren Lewis-Aciditäten und höheren Stabilitäten von Diazaphospholenium- im Vergleich zu nicht-konjugierten Phosphenium-Ionen und ermöglichten darüber hinaus die Bestimmung von Gleichgewichtskonstanten von P–Cl-Dissoziationsreaktionen. Die Ergebnisse zeigen im Einklang mit Konduktivitätsmessungen, daß P-Chlor-Diazaphospholene in Lösung nur zu einem geringen Grad dissoziiert sind. Ausgehend von diesen Befunden wird die bemerkenswerte Solvatochromie der NMR-Verschiebungen dieser Verbindungen einer solvensabhängigen Polarisation der P-Cl-Bindung und nicht einer Verschiebung des Dissoziationsgleichgewichtes zugeschrieben.*

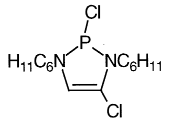
Even if a stabilizing effect of the double bond in type **A** phosphenium ions is undebatable, there is some controversy about its magnitude and influence on molecular structures. Thus, the presence of a remarkably long P–Cl bond (2.75 Å) in the chlorophosphane **1a** was attributed to a high degree of aromatic stabilization in the 1,3,2-diazaphospholene ring and lead the authors to formulate this compound as an ionic phosphenium salt **2a**[Cl].[13,16] On the other hand, compound **3b** (C_6H_{11} = cyclohexyl; P–Cl 2.42 Å)[17] was unmistakably addressed as a covalent species, and the bond lengthening with respect to compounds such as $(Me_2N)_2PCl$ (2.180(4) Å)[18] was attributed to hyperconjugation between the nitrogen lone pairs and the σ*(P–Cl) orbital.[17] Even for **2a**[Cl], the large deviation of the ^{31}P NMR chemical shift from that of ionic hexafluorophosphates or tetrachlorogallates **2a**[X] (X = BF_4, $GaCl_4$) suggested that in solution covalently interacting ion pairs rather separated ions are present.[13]



1a



2a[X]



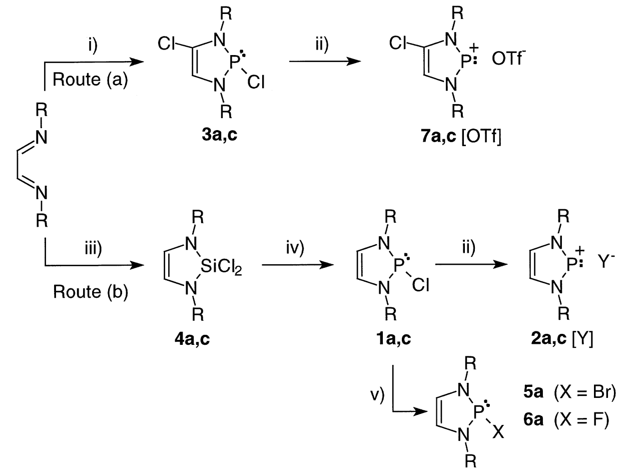
3b

In a recent theoretical study of stability and electrophilicity of phosphenium ions we have established that the energetic effect of π delocalization in 1,3,2-diazaphospholenium ions is of comparable magnitude to inductive substituent effects.[15b] In this light, concise assessment of the relation between π delocalization and electrophilicity in cations such as **2a** and the peculiar bonding situation in the corresponding halogenophosphanes (**1a**) should improve the understanding of structures and reactivities of the phosphorus analogues of Arduengo carbenes. As the results might allow further conclusions about the reaction behavior of halogenophosphanes in general,[19] we felt that a more comprehensive study was of interest.

In order to identify and separate the influences of substituent effects and π delocalization, we synthesized an extended palette of 1,3,2-diazaphospholene systems with different substituents at the phosphorus (X = halide, nucleofugic anions), carbon (R = H, Cl), and nitrogen atoms (R = Mes, *t*Bu), and studied their structure and bonding by spectroscopic, structural, and theoretical methods. Relative electrophilicities were both estimated from computed cation stabilization energies[15] and determined experimentally from stability constants of donor–acceptor adducts with a Lewis base.[11d] The results allow a concise characterization of ionicity and self-ionization in 2-chloro-1,3,2-diazaphospholenes; this is considered fundamental for correct assessment of stability and reactivity of ionic phosphorus analogues of Arduengo carbenes.

Results

Syntheses: The main synthetic strategies[20] to λ3-1,3,2-diazaphospholene rings include base-induced addition of phosphorus trichloride to 1,4-diazadienes to give 2,4-dichloro-1,3-dialkyl(diaryl)-substituted derivatives (Scheme 1, route a),[12,21]



Scheme 1. Synthesis of 2-halogeno-1,3,2-diazaphospholenes and 1,3,2-diazaphospholenium cations. R = *t*Bu (**1a**–**7a**), Mes (**1c**–**7c**). i) PCl_3/NEt_3; ii) Me_3SiOTf or $AgBF_4$ ($Y = BF_4$); iii) $HSiCl_3$/diazabicyclooctane; iv) PCl_3; v) AgF (Y = F), Me_3SiBr (Y = Br).

or metathesis of PCl_3 with 2,2-dichloro-1,2-dihydro-1,3,2-diazasiloles[13, 16a] or diazadiene dianions[16b] to give 2-chloro-1,3-dialkyl-substituted compounds (Scheme 1, route b). For the present study, we used both routes to obtain in addition to the known compounds **1a**[13, 16a] and **3a**[21] the *N*-mesityl derivatives **1c** and **3c** (Scheme 1). The required sila-heterocycles **4a** and **4c** were prepared as published by Karsch.[22] The phosphorus heterocycles were isolated as crystalline solids after filtration, evaporation of solvents, and recrystallisation (THF/hexane or toluene). In contrast to previous reports,[13, 16a] we found compound **1a** sufficiently volatile to be purified by sublimation.

2-Fluoro and -bromo-1,3,2-diazaphospholenes were prepared by treating **1a** with trimethylsilyl bromide in THF, or with silver fluoride in CH_2Cl_2. The 2-bromo derivative **5a** was isolated by the same procedure as **1c**, and the fluoro compound **6a** was purified by vacuum sublimation. Similar halogen exchange reactions were observed by ^{31}P NMR spectroscopy for **1c**, but no pure compounds were isolated, as even repeated recrystallization failed to remove all byproducts. Chloride abstraction from **1a**, **1c**, **3a**, or **3c** by metathesis with silver tetrafluoroborate or trimethylsilyl triflate gave the phosphenium salts **2a**[BF_4], **2c**[OTf], **7a**[OTf], and **7c**[OTf], which were precipitated as crystalline solids after layering the reaction mixtures with hexane.

All prepared diazaphospholene derivatives are colorless to light yellow solids that are thermally stable, but sensitive to air and moisture. All compounds were characterized by analytical and spectroscopic methods, and several of them by means of X-ray crystallography.

Crystal structure studies: Single-crystal X-ray structure determinations were carried out for compounds **1a**,[23] **1c**, **2a**[BF_4], **6a**, **7a**[OTf], and **7c**[OTf]. Important bond lengths are listed in Table 1. The fluorine atoms in the anion of **2a**[BF_4] are disordered, but this did not preclude determination of accurate structural data for the cation. The literature data for compounds **1a** ($x\,C_7H_8$),[13] **2a**[PF_6],[13] **3b**,[17] and **7b**[$SbCl_6$][12] are also included in Table 1 for comparison.

The molecular structures of the salts **2a**[BF_4], **7a**[OTf], and **7c**[OTf] display close similarities to those of **2a**[PF_6][13] and **7b**[$SbCl_6$].[12] The individual cations exhibit no interionic contacts shorter than the sum of van der Waals radii and feature planar rings and practically identical endocyclic bond lengths and angles. It has been pointed out[12, 13, 16b] that the observed bond length equalization (all endocyclic distances are intermediate between single and double bonds) provides strong evidence for the presence of π-electron delocalization in the ring. Further support for this view is gained from a comparison of endocyclic and exocyclic C–N bond lengths in **7c**: the exocyclic bonds (average length $d_{avg} = 1.462$ Å) are considered pure single bonds, since π interactions between the orthogonal mesityl and diazaphospholene rings vanish because of symmetry reasons, and the relative shortening of the endocyclic bonds (1.376 Å) may then be attributed to partial double-bond character arising from π delocalization in the diazaphospholene ring. Similar considerations for the cations **2a**, **7a**, or **7b** cannot be drawn due to the different hybridization at exocyclic and endocyclic carbon atoms.

The halogenodiazaphospholenes **1c** (Figure 1) and **6a** (Figure 2) occur in the crystal as neutral molecules with

Table 1. Relevant bond lengths, bond angles, and torsion angles [distances in Å, angles in°] of 1,3,2-diazaphospholenes (**1a**, **1c**, **3b**, and **6a**) and 1,3,2-diazaphospholenium cations (**2a** and **7a**–**c**). The molecular structures of **3b** and **7b** are identical to those of **3a**, and **7a**, except that R = cyclohexyl instead of *tert*-butyl.

	P–X	P–N	N–C	C–C	N–C_{ex}[a]	N-P-N	α[b]
6a	1.6544(14)	1.672(2) 1.6721(19)	1.415(3) 1.415(3)	1.336(3)	1.489(3) 1.493(3)	90.45(10)	9.9
1a · C_7H_8[13]	2.759(2)	1.660(2) 1.662(2)	1.379(3) 1.389(3)	1.347(3)	1.508(3)	90.41(10)	4.9
1a	2.6915(4)	1.6628(8) 1.6651(8)	1.3912(12) 1.3913(12)	1.3485(14)	1.4967(12) 1.4999(12)	90.57(4)	6.7
2a[PF_6][13]	–	1.661(2) 1.662(3)	1.376(3) 1.377(3)	1.341(4)	1.502(4) 1.503(4)	90.71(11)	(planar)
2a[BF_4]	–	1.6579(14) 1.6654(14)	1.368(2) 1.370(2)	1.353(2)	1.507(2) 1.513(2)	90.38(7)	1.2
1c	2.3241(4)	1.6734(10) 1.6750(11)	1.4057(15) 1.4015(16)	1.3378(18)	1.4460(15) 1.4426(15)	89.69(5)	7.2
7c[OTf]	–	1.6662(15) 1.6708(15)	1.374(2) 1.378(2)	1.351(2)	1.460(2) 1.464(2)	89.55(7)	1.9
7a[OTf]	–	1.6580(16) 1.6713(16)	1.369(2) 1.378(2)	1.353(3)	1.509(2) 1.516(2)	91.05(8)	0.1
7b[$SbCl_6$][12]	–	1.656(4) 1.673(4)	1.363(6) 1.370(6)	1.351(7)	1.487(6) 1.502(6)	90.0(2)	(planar)
3b[17]	2.416(2)	1.587(3) 1.672(3)	1.390(6) 1.396(5)	1.320(6)	1.472(5) 1.480(5)	90.3(2)	8.1

[a] Exocyclic N–C bond length; [b] Average value of the two CCNP torsion angles.

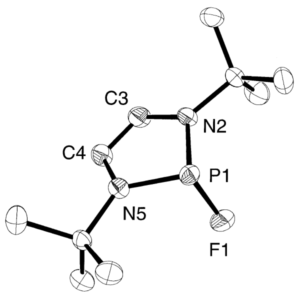


Figure 1. Molecular structure of **6a** in the crystal, ORTEP view thermal ellipsoids are at the 50% probability level, H atoms omitted for clarity; selected bond lengths and angles are given in Table 1.

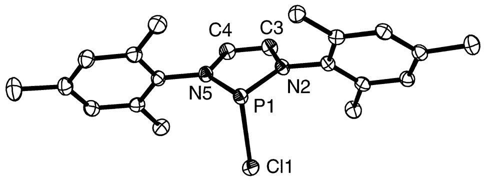


Figure 2. Molecular structure of **1c** in the crystal, ORTEP view thermal ellipsoids are at the 50% probability level, H atoms omitted for clarity; selected bond lengths and angles are given in Table 1.

covalent phosphorus–halogen bonds. Whereas the P–F bond length in **6a** is close to a single bond (1.583 Å)[24], the P–Cl bond length in **1c** (2.3241(4) Å) lies between a normal covalent bond (>2.18 Å)[18, 25] and the P–Cl bonds in **3b** (2.416(2) Å)[12] and **1a** (2.6915(4) Å; 2.759(2) Å in **1a**$\cdot x C_7H_8$)[13]. The diazaphospholene rings display envelope conformations in which the displacement of the phosphorus atom from the C_2N_2 plane increases from **1c** (0.20 Å) to **6a** (0.27 Å). The phosphorus atoms are pyramidal (sum of bond angles 295/294° for **1c**/**6a**) and the halogen atoms occupy flagpole positions. Somewhat surprisingly, these substantial constitutional changes with respect to the cations **2a**, **7a**, and **7c** have almost no effect on the endocyclic bond lengths. The P–N bonds ($d_{avg} = 1.674/1.672$ Å for **1c**/**6a**) are slightly longer and the C–C bonds (1.338/1.336 Å for **1c**/**6a**) shorter than in **2a** (P–N 1.662, C–C 1.347 Å), but the deviations are almost insignificant. The C–N bonds ($d_{avg} = 1.404/1.415$ Å for **1c**/**6a**) are likewise longer than in **2a** ($d_{avg} = 1.375$ Å), but fall short of a single bond (cf. 1.462 Å for the exocyclic C–N bonds in **7c**[OTf]). The exocyclic C–N bons lengths in **1c** still exceed the endocyclic ones, but the difference is less than half as large as in **7c**. This is pertinent with the view that cyclic π-electron conjugation is reduced, but not completely interrupted, upon P–Cl bond formation (vide infra for a further bonding discussion).

Comparison of the structural parameters of **1a** and the cation **2a** with those of isoelectronic silylenes and the 1,3,2-diazaphospholane $(CH_2N(t\text{Bu}))_2PCl$ has been used to gauge the degree of aromaticity in these molecules and to attest the ionic nature of **1a**.[13, 16] The present structural study of a larger number of diazaphospholene systems sheds new light on the justification of this approach and, in fact, reduces much the impact of structural arguments for a bonding discussion. Thus, comparison of the structures of the cations **2a** and **7a**–**c** with those of the neutral species **1c**, and **3b** reveals that apart from small variations in C–N bond lengths and slight folding of the ring, the structural response following the attachment of a substituent at phosphorus is not very substantial. As a consequence, the change in C–N bond lengths between **1a** ($d_{avg} = 1.391$ Å) and the cation **2a** ($d_{avg} = 1.375$ Å), although small on an absolute scale, is still half as large as that between **2a** and covalent **6a** ($d_{avg} = 1.415$ Å). This suggests that the structural, and presumably electronic, perturbation of the diazaphospholene unit by the chloride ion in **1a** is not negligible and contradicts the formulation of this compound as ionic. Structure correlation between the *P*-chlorodiazaphospholenes **1a**, **1c**, and **3b** reveals further that the unusually long P–Cl bond in **1a** is unique and that variations in endocyclic bond lengths follow neither a common trend nor exhibit a simple relation to the P–Cl bond length. In the light of these findings, the P–Cl bond lengthening in **1a** cannot be considered as an intrinsic consequence of aromaticity, but must be attributed to substituent influences in this special compound.

Spectroscopic investigations and conductometric measurements: Systematic spectroscopic and conductometric studies on diazaphospholene systems were carried out with the main focus to elucidate the nature of the phosphorus–halogen bonds not only in the solid state, but also in solution and the gas phase. Spectroscopic data of previously known compounds (e.g. **1a**) were included as far as they had not been reported elsewhere.

The ^{31}P NMR chemical shifts of the new *P*-halogenodiazaphospholenes **1c**, **5a**, and **6a** fall in the expected range for covalent compounds of the type $XP(NR_2)_2$.[26] Solvent dependent shifts of $\delta\,^{31}$P similar to those noted for **1a**[16a] and 2-chloro-1,3-dibutyl-4,5-dimethyl-1,3,2-diazaphospholene (**8**)[27] were observed for the *P*-chloro(bromo)-compounds **1c**, **3a**, **3c**, and **5a**, but not for the fluoro compound **6a**.[28] The magnitude of solvatochromic shifts for **1a**, **1c**, and **3a** follows the order of increasing P–Cl bond length in the solid state. Adopting the idea of solvent-induced ionization[16a, 27] as the source of the changes, one would expect that temperature- or concentration-dependent shifts of dissociation equilibria have marked effects on observable chemical shifts. Detailed ^{31}P NMR studies of **1a** and **1c** revealed that this is not the case: $\delta\,^{31}$P values vary only insignificantly over a large range of temperatures (+30 to −80 °C) and concentrations (0.02 to 1 M), and spectra recorded at low temperatures gave no evidence for dynamically induced line broadening, which had been observed for other P–Cl bond-dissociation equilibria.[29]

The nature of the P–X bonds in *P*-fluoro and *P*-chlorodiazaphospholenes was further illuminated by studies of halogen NMR spectra of **1a**, **1c**, **3a**, and **6a**. The covalent character of the P–F bond in **6a** follows directly from the large scalar coupling ($^1J_{PF} = 1070$ Hz) between both nuclei. Similar couplings between ^{31}P and ^{35}Cl (75.53%, $I = 3/2$) or ^{37}Cl (24.47%, $I = 3/2$) nuclei are normally unobservable owing to rapid quadrupolar relaxation of the halogens,[30] but a distinction between ionic or covalent nature of P–Cl bonds is still feasible by comparison of ^{35}Cl linewidths;[30] chlorine nuclei in covalent bonds display generally broad lines with halfwidths of some kHz, since here quadrupolar relaxation is effectively driven by a large local electric-field gradient, whereas in chloride anions the vanishing electric-field gradient makes quadrupolar relaxation inefficient and leads to narrow lines with halfwidths of a few Hz. Measurement of ^{35}Cl NMR spectra (30 °C, CH_3CN) for **1a**, **1c**, and **3a** revealed that the signal of **1c** is too broad to be detected, whereas **3a** and **1a** display each a single resonance, which in the case of **3a** cannot be unambiguously assigned to one of the two chlorine atoms (Figure 3a and 3b). The observed linewidth of **1a** ($\Delta w_{1/2} =$ 3.1 kHz) is lower than that of **3a** ($\Delta w_{1/2} = 6.8$ kHz), but still exceeds that of the anion in $[Et_4N][Cl]$ ($\Delta w_{1/2} = 25$ Hz, Figure 3c) by two orders of magnitude. Consequently, none of the three diazaphospholenes shows characteristics of a genuine ionic species, but the decrease in ^{35}Cl linewidths again correlates with increasing P–Cl bond lengths and suggests growing ionic character of the P–Cl bonds in the order **1c**, **3a**, **1a**.

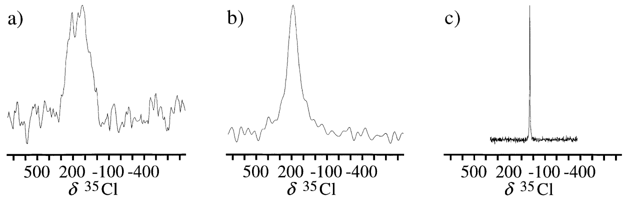


Figure 3. ^{35}Cl NMR spectra of a) **3a** (ca. 1M in CH_3CN, 30 °C, fit to a single Lorentzian line yielded $\delta^{35}Cl = 161$, $\Delta w_{1/2} = 6.8$ kHz); b) **1c** (1M in CH_3CN, 30 °C, $\delta^{35}Cl = 194$, $\Delta w_{1/2} = 3.1$ kHz); c) $[Et_4N][Cl]$ (0.1M in CH_3CN, 30 °C, $\delta^{35}Cl = 36$, $\Delta w_{1/2} = 0.025$ kHz).

In addition to NMR spectroscopy, vibrational spectroscopy was tracked as a further source of information on phosphorus–halogen bonding. A comparison of IR and Raman spectra of the *N-tert*-butyl-substituted derivatives **1a**, **5a**, **6a**, and **2a**[BF_4] revealed that apart from the bands of B–F and P–F stretch vibrations in **2a**[BF_4] ($\nu(BF) = 1030$, 1046 cm^{-1}) and **6a** ($\nu(PF) = 617$ cm^{-1}) the spectra are similar, but not identical,[31] thus disproving that all compounds can be described as salts with the same cation. While interpretation of differences in the fingerprint region was unfeasible as expected for molecules of this size, a diagnostically relevant change was found in the continuous variation of the characteristic $\nu(C{=}C)$ frequency (Table 2). In accord with computational studies this effect is explained as a consequence of increasing covalent P–X bond orders in the series X = (BF_4), Br, Cl, F, which leads to increased π-electron localization and concomitant strengthening of the C=C bond. The computational results indicate further that the absence of characteristic bands attributable to ν(PCl) or ν(PBr) in **1a** and **5a** is still compatible with a covalent nature of the bonding and owes to both the weakness of the bond, which presumably shifts the frequency into the barely accessible spectral region below 250 cm^{-1}, and to concealment of the spectral transition by coupling with skeletal vibrations. A bond-weakening effect is also evident for the P–F bond in **6a** whose frequency is considerably red-shifted with respect to the expectation range ($\nu(PF) = 770-760$ cm^{-1}[32]) for trivalent phosphorus compounds.

Table 2. Experimental and calculated (at the b3lyp/6-31(+)g* level) vibrational frequencies [cm^{-1}] of $\nu(C{=}C)$ in 1,3,2-diazaphospholene compounds X-P(N(tBu)CH)$_2$.

	2a[BF_4]	**5a**	**1a**	**6a**
X	BF_4	Br	Cl	F
exptl (IR)		1552	1560	1625
exptl (Raman)	1527	1551	1559	
calcd	1567[a]	1632	1636	1661

[a] Values refer to the isolated cation.

The occurrence of molecular ions in the mass spectra of **1a**, **1c**, **5a**, and **6a** indicates that in all cases intact halogenodiazaphospholene molecules are present in the gas phase. The intensities of the molecular ions decrease with increasing atomic mass of the halogen. Fragmentation proceeds in **6a** nearly exclusively under cleavage of isobutene and conservation of the P–F bond, whereas **1a**, **1c**, and **5a** decay predominantly through extrusion of a halogen radical to give the cations **2a** and **2c**, of which **2a** eliminates further isobutene fragments. Altogether, these findings suggest that the stabilities of the P–halogen bonds decrease in the order $P{-}F \gg P{-}Cl > P{-}Br$.

Considering that dissociation of halogenodiazaphospholenes should affect the electric conductivity of the solutions, we measured molar conductivities Λ_m for **1a**, **1c**, **2a**[OTf], and **2c**[OTf] and compared the data with those of covalent (iPr$_2$N)$_2$PCl (**9**) and the salts [(iPr$_2$N)$_2$P][OTf] (**10**) and $[Et_4N]$[OTf] (Table 3). The molar conductivities of **2a**[OTf] and **2c**[OTf] are similar to those of **10** and $[Et_4N]$[OTf]; this leads to the assignment of these compounds as 1:1 electrolytes. In contrast, the values of Λ_m for **1a**(**1c**) are lower than those of **2a**(**2c**) [OTf] by a factor of 13(31). We conclude therefore that even if **1a** is a slightly stronger electrolyte than **1c**, both solutions contain mainly covalent molecules or strongly associated contact ion pairs. The higher conductivities of the studied phosphenium triflates relative to $[Et_4N]$[OTf] suggest that the strong interionic interactions that have been observed for a diaminophosphenium triflate[33] are absent for the compounds studied here.[34]

Table 3. Molar conductivities [Ω^{-1} cm^2 mol^{-1}] of chlorophosphanes **1a**, **1c**, and **9**, and phosphenium salts **2a**(**2c**)[OTf], **10**[OTf], and $[Et_4N]$[OTf] (all 0.01M solutions in CH_2Cl_2, 295 K).

	1a	**2a**[OTf]	**1c**	**2c**[OTf]	**9**	**10**	$[Et_4N]$[OTf]
Λ_m	0.09	1.13	0.04	1.25	0.01	1.67	0.96

Computational studies: Computational studies were performed with the aim of a fundamental comprehension of substituent influences on structure and energetics in diazaphospholene compounds, and a simulation of thermodynamic cycles[13, 15b, 35] that allow us to estimate the stabilities of the corresponding cations.[15a] The chosen theoretical model implies evaluation of energies and NBO population analyses[36] at the b3lyp/6-31 + g(d) + zpe level. Molecular geometries have been energy-optimized at the same level and are minima on the energy hypersurface according to frequency analyses. A comprehensive listing of results is given as Supporting Information.

The computed structures of the cations **2a**, **2d**, **2e**, and **7e** exhibit planar rings whose endocyclic bond lengths are practically independent of the substitution pattern. The results of NBO population analyses (Table 4) confirm, in accord with previous studies,[13, 15b] the presence of weak π delocalization between the C=C double bond and the heteroallylic NPN fragment in the five-membered ring. Replacement of NH substituents in **2e** by electron-releasing alkyl groups (**2a**, and **2d**) increases the shift of π electron density from the nitrogen lone pairs into the vacant phosphorus p orbital and, therefore, adds to the dative stabilization of the phosphenium center. Attachment of a chlorine to an endocyclic carbon atoms leaves the electron distribution in the diaminophosphenium fragment essentially undisturbed, but weakens the C=C double bond.

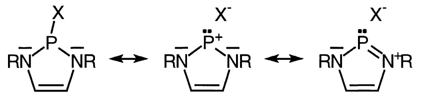
Table 4. Results of NBO population analysis at the B3LYP/6-31(+)g(d) level in 1,3,2-diazaphospholene compounds X–P(N(R)CH)$_2$; q(X) denotes the halogen atomic charge, and n(p$^\pi$) the electron population of the p$^\pi$ orbital at the phosphorus atom in the cations.

				Wiberg Bond Indices				
	R	X	q(X)	P–X	P–N	N–C[b]	C=C	n(p$^\pi$)
1a	tBu	Cl	–.58	0.50	0.90	1.09	1.70	
1d	Me	Cl	–.52	0.59	0.88	1.08	1.71	
1e	H	Cl	–.49	0.64	0.90	1.09	1.73	
3a[a]	tBu	Cl	–.55	0.50	0.88	1.09	1.64	
5a	tBu	Br	–.57	0.49	0.90	1.10	1.68	
5d	Me	Br	–.50	0.59	0.88	1.09	1.70	
5e	H	Br	–.47	0.64	0.90	1.10	1.72	
6a	tBu	F	–.64	0.52	0.86	1.06	1.74	
6d	Me	F	–.63	0.54	0.85	1.06	1.74	
6e	H	F	–.63	0.56	0.88	1.08	1.75	
2a	tBu	–	–	–	1.12	1.22	1.54	0.96
2d	Me	–	–	–	1.02	1.22	1.54	0.95
2e	H	–	–	–	1.05	1.23	1.54	0.86

[a] -CH=CCl- instead of -CH=CH-; Wiberg bond indices for P–N and N–C bonds denote the average values for the two different bonds. [b] Values for single bonds (e.g., for the exocyclic C–N bonds) are in the range 0.86–0.96.

The 2-halogenodiazaphospholenes **1a**, **1d**, **1e**, **5a**, **5d**, **5e**, **6a**, **6d**, and **6e** appear, according to the computations, as C_s-symmetric molecules, whose folded rings display the same conformations as were found in the crystal structure studies. Only minor deviations from C_s symmetry were obtained for the 4-chloro-substituted compounds **3a** and **3e**. The calculated P–X bond lengths in **1e** (P–Cl 2.297 Å) and **5e** (P–Br 2.490 Å) exceed those in XPH$_2$ (P–Cl 2.111, P–Br 2.277 Å at the same level of theory) by 9% and XP(NH)$_2$(CH$_2$)$_2$ (P–Cl 2.256, P–Br 2.442 Å) by 2%, and increase further upon replacement of the NH substituents by electron-releasing methyl (P–Cl 2.344 Å, **1d**) or *tert*-butyl groups (P–Cl 2.433 Å, **1a**). The bond lengthening is accompanied by an increase of negative charge on the halogen atoms and a concomitant decrease of P–X bond orders (Table 4); this suggests that the ionic contribution to the P–X bonds is higher in **1e**/**5e** than in XP(NH)$_2$(CH$_2$)$_2$ (X = Br,Cl) and is further enhanced by σ-donating substituents at the nitrogen atoms. The lengthening of P–F bonds in **6e** (1.694 Å) with respect to the reference compounds FP(NH)$_2$(CH$_2$)$_2$ (1.680 Å) and FPH$_2$ (1.650 Å) is less pronounced (1% and 3%), and N-alkylation induces much smaller changes of P–F bond lengths [P–F 1.706 (**6d**, R = Me), 1.722 Å (**6a**, R = tBu)] and bond orders, and has nearly no effect on the charge on the fluorine atom.

The attachment of P-halogen substituents renders the endocyclic P–N and C–N bonds longer and the C–C bonds shorter than in the cations **2a**, **2d**, and **2e**, but even though these changes are accompanied by parallel variations in bond orders, the Wiberg bond indices for the C–N and P–N bonds remain larger than expected for pure single bonds. This is good evidence for the presence of residual π-electron delocalization and can be rationalized in terms of hyperconjugation of the 6π system in the C$_2$N$_2$ fragment with the energetically low-lying σ*(P–X) orbital.[17] Such an interaction is expressed in the language of valence bond (VB) theory by a "bond/no-bond resonance" as shown in Scheme 2, the driving force of which is presumably the reduction of the strong C–N antibonding interaction in the HOMO of the C$_2$N$_2$ fragment, which is isoelectronic to a butadiene dianion. All further changes in substitutent patterns of 2-halogenodiazaphospholenes leave the endocyclic bond lengths practically invariant and induce only minor shifts of bond indices.



Scheme 2.

The substituent influences on the stability of the diazaphospholenium ions **2a**, **2d**, and **2e** can be assessed from the energies ΔE^{tr}(X)[15] (Figure 4) of the isodesmotic fluoride-(X = F) or chloride-transfer reactions (X = Cl) shown in Scheme 3.[37] The excess stabilization energy $\Delta\Delta E^{tr}$(X) of the cation **2e** (11.0, 10.2 kcal mol^{-1} for X = F, Cl), which

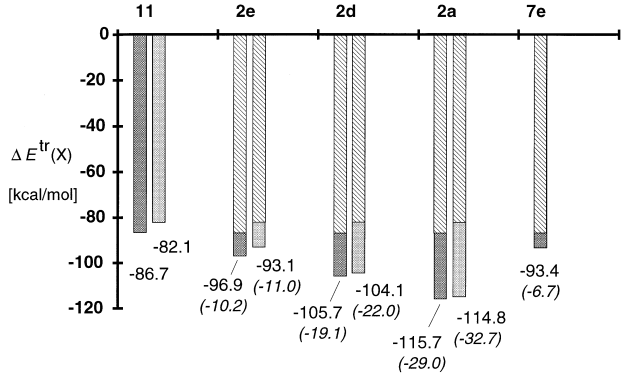
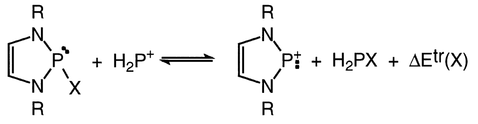


Figure 4. Computed reaction energies ΔE^{tr}(X) [kcal mol^{-1}] at B3LYP/6-31(+)g(d) + ZPE level for the isodesmotic halide-transfer reactions given in Scheme 3. The corresponding reaction energy for the non-conjugated cyclic cation [P(NHCH$_2$)$_2$]$^+$ (**11**) is included for comparison. Dark and light grey columns correspond to X = Cl and F, respectively; values in parentheses denote excess stabilization energies $\Delta\Delta E^{tr}$(X).



Scheme 3. Isodesmotic halide transfer reactions (X = F, Cl, Br)

denotes the increase in $\Delta E^{tr}(X)$ with respect to the C–C-saturated $[P(NH)_2(CH_2)_2]^+$ and is a measure of aromatic stabilization,[15b] compares with the additional stabilization induced by introduction of *N*-methyl ($\Delta\Delta E^{tr}(X) = 11.0$, 8.8 kcal mol^{-1} for X = F, Cl) or *N-tert*-butyl groups ($\Delta\Delta E^{tr}(X) = 21.7$, 18.8 kcal mol^{-1} for X = F, Cl). Attachment of a chlorine in the 4-position diminishes $\Delta E^{tr}(Cl)$ slightly by 3.5 kcal mol^{-1}. Computation of standard (free) reaction enthalpies and entropies for the P–X bond dissociation in the gas phase (see Supporting Information) revealed that the increase in cation stabilities with increasing size of the *N*-alkyl group is related to variations in ΔH, while ΔS remains essentially unchanged. This suggests that the observed trends are attributable to enhanced dative stabilization of the phosphenium center and that conformational strain which might favor P–X dissociation in the *N*-*t*Bu derivatives **1a** and **6a** is presumably of little importance.

Formation of Lewis base adducts: The concept of cation stabilization energies relies on the idea that more stable cations are less liable to form donor–acceptor adducts with nucleophilic counterions or neutral donors.[15b] For a generalized reversible reaction between a posphenium ion and a nucleophile [Eq. (1)], increasing cation stability is associated with a shift of the equilibrium to the left and thus a decrease of the value of K_1. On this basis, measurement of equilibrium constants for reactions of different cations with a common nucleophile has been used for the experimental determination of relative cation stabilities.[11d] Recent work by Bertrand has established that the same donor–acceptor adducts are also accessible from the reaction of covalent chloro-phosphanes with strong nucleophiles such as 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).[19a] A general reaction of this type can be formulated as Equation (2) and is characterized by an equilibrium constant K_2.

$$R_2P^+OTf^- + DBN \rightleftharpoons [R_2P \leftarrow DBN]^+OTf \qquad K_1 = [R_2P^+ \leftarrow DBN]/[DBN][R_2P^+] \tag{1}$$

$$R_2P^+Cl^- + DBN \rightleftharpoons [R_2P \leftarrow DBN]^+Cl^- \qquad K_2 = [R_2P^+ \leftarrow DBN][Cl^-]/[DBN][R_2PCl] \tag{2}$$

$$R_2P^+Cl^- \rightleftharpoons R_2P^+ + Cl^- \qquad K_3 = K_2/K_1 \tag{3}$$

Measurement of the equilibrium constants K_1 and K_2 for reactions of diazaphospholenium triflates[38] and the corresponding chlorodiazaphospholenes with a common nucleophile offers now a possibility for the experimental evaluation of both relative stabilities of individual cations and the ionic or covalent nature of the P–Cl bonds. The latter is based on the perception that for an ionic chlorodiazaphospholene Equations (1) and (2) are equivalent, and K_1 and K_2 therefore identical. On the other hand, significantly deviating values indicate a covalent contribution to the P–Cl bonding whose extent can be estimated from the equilibrium constant K_3 of the hypothetical bond dissociation reaction [Eq. (3)]. Since Equation (3) is equivalent to the difference of Equations (2) – (1), the value of K_3 is easily obtained as the quotient of K_2 and K_1.

Our studies revealed that both diazaphospholenium triflates and chlorodiazaphospholenes react with nucleophilic amidines such as DBN or DBU to give equilibrium mixtures of the starting materials and 1:1 donor–acceptor adducts. Owing to dynamic exchange between the free electrophiles and the adducts, ^1H NMR spectra of these mixtures displayed only signals attributable to the population weighted average of the individual components at ambient temperature. This behavior enabled us to monitor the changes in molar fractions of the reactants during titrations of the diazaphospholene compounds versus DBN by recording the shift of suitable ^1H signals (Figure 5), and to obtain values for the equilibrium constants K_1 and K_2 from fits of these data to an appropriate formula (Table 5, see Experimental Section for details).

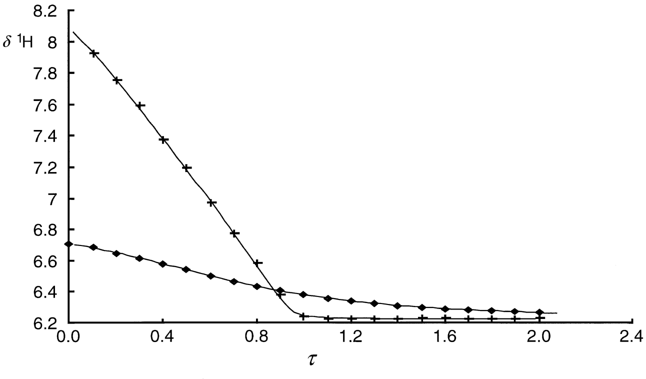


Figure 5. Change of $\delta\,^1H$ for the 4-H proton at the diazaphospolene ring during the titration of **3c** (diamonds) and **7c** (crosses) with DBN. The symbols denote the experimetnally observed chemical shifts, and τ indicates the degree of titration. The solid lines were obtained from a fit of the experimental data to a theorectical expression, by using the formula given in the Experimental Section, and yielded the values for K_1 and K_2 given in Table 5.

Comparison of K_1 values revealed **7a** to be a stronger electrophile than **2a**, in agreement with the trend in computed cation stabilities, while **2a** and **2c** have comparable electrophilicities. The different habits of the titration curves for corresponding pairs of diazaphospholenium triflates and chlorides revealed immediately that the latter are much weaker electrophiles than the cations. The computed values of the equilibrium constants K_3 for the P–Cl bond dissociation are in the order of 10^{-2}–10^{-3} L mol^{-1} and suggest that the ionic contribution to the bonding amounts only to few percent, thus agreeing with the measured conductivities.

In order to compare the electrophilicities of diazaphospholenium cations and acyclic phosphenium ions, we attempted as well to measure equilibrium constants for the formation of DBN adducts of $(iPr_2N)_2PCl$ (**9**) and $[(iPr_2N)_2P][OTf]$ (**10**[OTf]). In both cases it turned out that the equilibria were shifted almost completely to the side of the adducts, but

Table 5. Experimental equilibrium constants (estimated standard deviations in parentheses) for the Lewis acid/base and P–Cl bond dissociation reactions shown in Equations (1)–(3).

R_2P–X	$[R_2P]^+$	K_1 [mol^{-1}l]	K_2	K_3 [moll^{-1}]
3a	**7a**	$16(5) \times 10^3$	6.9(4)	$0.43(17) \times 10^{-3}$
1a	**2a**	$1.6(2) \times 10^3$	3.5(2)	$2.2(4) \times 10^{-3}$
1c	**2c**	$1.1(2) \times 10^3$	5.4(4)	$4.9(13) \times 10^{-3}$

further evaluation of the titration curves was prevented by the failure to quantify the equilibrium concentrations of free **9**, **10**, and DBN in the presence of a large excess of donor–acceptor complex.[39] Even if quantitative comparison of electrophilicities was not feasible, these experiments still confirmed that **10** is more electrophilic than a diazaphospholenium cation. This conclusion was further confirmed by the finding that reaction of the fluoro derivative **6a** with **10**[OTf] proceeded quantitatively by fluoride transfer to give the more stable cation **2a** and $(i\text{Pr}_2\text{N})_2\text{PF}$.

Discussion

Stability of 1,3,2-diazaphospholenium cations: Calculated stabilization energies and measured free enthalpies for the formation of DBN adducts confirm that 1,3,2-diazaphospholenium ions are, on the whole, more stable (i.e. less Lewis acidic) than nonconjugated diaminophosphenium ions. The computed stabilization energies of individual cations depend not only on the substituents at the nitrogen and carbon atoms as expected, but also on the nature of the leaving group. In particular, both group-transfer energies $\Delta E^{tr}(X)$ and excess energies $\Delta\Delta E^{tr}(X)$ that express the energetic effect of conjugation between the diaminophosphenium fragment and the C=C double bond, are much lower for halide- ($X = F$, Cl) than for hydride-transfer reactions ($X = H$).[15b, 40] We attribute this to i) the higher intrinsic polarity of a P–X ($X = F$, Cl), relative to a P–H bond, which facilitates bond heterolysis and ii) the additional stabilization of 2-halogenodiazaphospholenes by hyperconjugation. The slight decrease in $\Delta\Delta E^{tr}(X)$ for $X = Cl$ relative to that with $X = F$ (Table 4) is rationalized if one considers that the contribution of the ionic resonance structure in Scheme 2, and, hence, the stabilization of the *P*-halogenodiazaphospholene, increases with the extent of charge transfer from phosphorus to halogen.[41] Last, but not least, the inductive (de)stabilization of diazaphospholenium cations by σ-electron-donating (withdrawing) 2,5-alkyl or 4-Cl subsituents, respectively, confirms the view[15b] that the stabilities of aminophosphenium cations depend beside dative $N \rightarrow P$ π interactions also on the polarity of P–N σ bonds.

The similar significance of inductive substituent influences and π-conjugation effects for the total cation stabilization energies $\Delta E^{tr}(X)$ disagrees with the usual interpretation that aromatic stabilization is the main reason for the high stabilities of 1,3,2-diazaphospholenium systems,[13, 16] but is compatible with our earlier results[15b] that showed the stabilizing effect of 6π delocalization in diazaphospholenium ions to be lower than in the isoelectronic, and genuinely aromatic, phospholide anions. In regard of both the lower degree of equalization of bond lengths and bond orders relative to phospholides, and the results of NBO population analyses,[15b] the π-electron structure in 1,3,2-diazaphospholenium ions is better described in terms of a mixing of the occupied and empty π orbitals of a heteroallylic N_2P fragment under perturbation of an adjacent C=C double bond[15b] and not as a genuine aromatic π system. Similar bonding descriptions have been inferred for the isoelectronic 1,3-bisphosphoniophospholide[10d, 42] and 1,3,4,5-tetrazaphospholenium cations.[43]

The nature of the phosphorus–halogen bond in 2-halogeno-1,3,2-diazaphospholenes: The presented structural, spectroscopic, and computational studies culminate in a description of the phosphorus–halogen bonding in 2-fluoro(chloro)-1,3,2-diazaphospholenes as polar, covalent bonds that experience some weakening by $\pi(C_2N_2)-\sigma^*(P{-}X)$ hyperconjugation. The extent of this bond weakening is significantly less pronounced in the fluorine than the chlorine compounds, owing to the larger charge capacity and polarizability of chlorine which facilitates, according to the NBO population analyses, the charge transfer from phosphorus to the halogen and enhances the energetic efficiency of the hyperconjugation. The "softer" character of chlorine is also the reason for the marked influence of σ-donating(accepting) substituents at the carbon and nitrogen atoms on the P–X bonding; this is reflected in the extraordinarily large variability in observed P–Cl bond lengths. Quite remarkably, this high polarizability of the P–Cl bond induces no marked changes in the bonding in the diazaphospholene ring.

Even if the computational studies mirror the substituent-induced trends in P–Cl bond lengths and bond orders, they fail to reproduce the full range of P–X bond length variation. If one considers that the single molecules possess considerable dipole moments which may polarize the P–X bonds in neighboring molecules in the crystal, this discrepancy can be attributed to intermolecular contributions to the structural deformation that cannot be modeled by calculations referring to isolated molecules in the gas phase.[44] Following the same arguments, the large deviation between the two P–N bond lengths in crystalline **3b**,[12] which is likewise not reproduced by the calculations, may as well be explained by similar crystal effects.

The spectroscopic and conductometric studies as well as the investigation of Lewis acid/base equilibria indicate that 2-chlorodiazaphospholenes dissociate in solution only to a small extent and that a spontaneous cleavage of P–X bonds, as in ylide-substituted chlorophosphanes[29, 45] is not observed. Even if this result contradicts earlier conjectures,[13, 16] it complies with the higher stabilities of ylidyl-phosphenium ions as compared with diazaphospholenium cations.[15b] Although the main driving force for the partial ionization of halogenodiazaphospholenes lies without doubt in the extra stabilization of the formed cations by π-conjugation effects, the dissociation constant K_3 depends on substituent influences in both the cations and the neutral precursors. Owing to the complexity of these relationships and the scarcity of available data, no systematic trends were identified so far.

The contrary assessment of the degree of dissociation of chlorodiazaphospholenes also suggests a different interpretation of the solvatochromic behavior of ^{31}P chemical shifts, which was so far attributed to solvent-induced shifts of the dissociation equilibria.[13] Although our experiments confirmed the presence of ionic species in solution, the measured conductivities indicate that their concentrations are too low to account for the large variation in $\delta\,^{31}$P. A more satisfactory explanation is given if one assumes instead a polarization of the soft P–Cl bonds by polar solvent molecules that results in a solvent-dependent variation of bond lengths and bond strengths. Experimental proof for the occurrence of this effect in the solid state is given by the different P–Cl bond lengths of solvent-free **1a** and its toluene solvate (Table 1).

Conclusion

Structural, spectroscopic, and computational investigations lead to a differentiated picture of chemical properties, structures, and bonding situation in 1,3,2-diazaphospholene compounds. Diazaphospholenium triflates and tetrafluoroborates are ionic species whose cations feature weakly delocalized 6π-electron systems. The bonding situation resembles that of neutral analogues of Arduengo carbenes with Group 14 elements[5] and should not be described as genuinely aromatic. *P*-Halogenodiazaphospholenes are molecular species with covalent P–X bonds. Their bonding situation is characterized by residual π delocalization that arises from $\pi(C_2N_2)-\sigma^*(P{-}X)$ hyperconjugation and results in a weakening of P–X bonds. The effect is more pronounced in fluorine than in chlorine compounds and contributes to the amazing structural similarity of ionic and covalent diazaphospholene compounds. The low P–Cl bond strengths, easy tuning of bond lengths by inductive substituent effects, and solvent-induced bond polarization, which was identified as the source of the solvatochromaticity of ^{31}P chemical shifts, suggest that chlorodiazaphospholenes can be described in the sense of A. Haaland as donor–acceptor complexes[46] of a diazaphospholenium cation and a chloride anion.

Measurement of stability constants for adducts of 1,3,2-diazaphospholene chlorides and triflates with Lewis bases confirmed that the cations are more stable than saturated cyclic or acyclic diaminophosphenium ions and permitted for the first time the determination of equilibrium constants for P–Cl bond dissociation reactions. The results proved that 2-chloro-1,3,2-diazaphospholenes dissociate in solution only to a small extent.

Experimental Section

General remarks: All manipulations were carried out under dry argon. Solvents were dried by standard procedures. Compounds **1a**,[16a] **4a** and **4c**,[22] and **9** and **10**[47] were prepared as described. NMR spectra: Bruker AMX300 (^{1}H: 300.1 MHz, ^{31}P: 121.5 MHz, ^{13}C: 75.4 MHz, ^{15}N: 30.4 MHz, ^{35}Cl: 29.4 MHz) and Bruker AMX500 (^{19}F: 470.6 MHz); chemical shifts referenced to external TMS (^{1}H, ^{13}C), $MeNO_2$ ($\Xi = 10.136767$ MHz, ^{15}N), $CFCl_3$ ($\Xi = 94.094003$, ^{19}F), 85% H_3PO_4 ($\Xi = 40.480747$ MHz, ^{31}P), 0.1 M aqueous NaCl (^{35}Cl); positive signs denote shifts to lower frequencies, and coupling constants are given as absolute values; prefixes *i*-, *o*-, *m*-, *p*- denote atoms of mesityl substituents. In order to minimize spectral distortions arising from pulse ringdown effects, ^{35}Cl NMR spectra were recorded with a $90^\circ(x)-90^\circ(\phi)-90^\circ(x)$ aquisition(ϕ) pulse sequence in which the phase ϕ was changed between $\pm x$ for subsequent transients. MS: VG-Instruments VG 12-250. FT-IR spectra: Bruker IFS113V. Raman spectra: Bruker RFS100. Elemental analyses: Heraeus CHNO-Rapid. Melting points were determined in sealed capillaries. Conductance measurements were performed in CH_2Cl_2 at ambient temperature with a WTW LF330 conductometer and a probe cell with cell constant = 0.100.

2-Chloro-1,3-di-*tert*-butyl-1,3,2-diazaphospholene (1a): IR (CsI): 255 (w), 299 (w), 458 (w), 539 (s), 598 (w), 708 (m), 774 (m), 792 (s), 1024 (w), 1043 (w), 1081 (s), 1200 (s), 1234 (m), 1266 (m), 1369 (m) 1469 (m), 1560 (m), 2978 (m), 3073 cm^{-1} (m); Raman: 137, 255, 708, 1064, 1560, 2911, 2980, 3055 cm^{-1}; MS (20 eV, EI): m/z (%): 234 (4) $[M]^+$, 199 (31) $[M-Cl]^+$, 143 (16) $[M-Cl-C_4H_8]^+$, 87 (100) $[M-Cl,-2\,C_4H_8]^+$.

2-Chloro-1,3-dimesityl-1,3,2-diazaphospholene (1c): PCl_3 (5.50 g, 40.0 mmol) was added to a solution of **4c** (14.00 g, 35.8 mmol) in toluene (500 mL), and the mixture was refluxed for 7 d. After cooling and filtration over celite, the filtrate was evaporated in vacuo. The residue was dissolved in CH_2Cl_2 (20 mL), and the solution then treated with hexane (200 mL). The product isolated as light yellow crystals, which were separated by filtration, washed with hexane, and dried in vacuo (yield 5.40 g (58%)). M.p. 204–206 °C; ^{1}H NMR ($CDCl_3$, 303 K): $\delta = 6.97$ (s, 2H; *m*-CH), 6.42 (s, 2H; =CH), 2.41 (s, 12H; *o*-CH_3), 2.31 (s, 6H; *p*-CH_3); $^{13}C\{^{1}H\}$ ($CDCl_3$): $\delta = 138.1$ (d, $^{5}J_{PC} = 2.3$ Hz; *p*-C), 136.8 (d, $^{3}J_{PC} = 4.6$ Hz; *o*-C), 135.1 (d, $^{2}J_{PC} = 9.9$ Hz; *i*-C), 130.5 (d, $^{4}J_{PC} = 1.1$ Hz; *m*-C), 120.2 (d, $^{2}J_{PC} = 8.9$ Hz; =CH), 21.3 (d, $^{6}J_{PC} = 0.8$ Hz; *p*-CH_3), 19.4 (d, $^{4}J_{PC} = 2.7$ Hz; *o*-CH_3); $^{31}P\{^{1}H\}$ (toluene): $\delta = 141.5$; $^{31}P\{^{1}H\}$ (CH_2Cl_2): $\delta = 149.2$; MS (16 eV, EI): m/z (%): 358 (30) $[M]^+$, 323 (100) $[M-Cl]^+$; elemental analysis calcd (%) for $C_{20}H_{24}ClN_2P$ (358.85): C 66.94, H 6.74, N 7.81; found C 65.83, H 6.82, N 7.51.

2,4-Dichloro-1,3-di-*tert*-butyl-1,3,2-diazaphospholene (3a) and 2,4-dichloro-1,3-dimesityl-1,3,2-diazaphospholene (3c): Compounds **3a** and **3c** were prepared in analogy to 2,4-dichloro-1,3-bis-(2,6-dimethylphenyl)-1,3,2-diazaphospholene.[20]

*Compound **3a***: Yield 41%; m.p. 95–97 °C; ^{1}H NMR ($CDCl_3$): $\delta = 6.67$ (s, 1H; =CH); 1.76 (s, 9H; $C(CH_3)_3$), 1.62 (s, 9H; $C(CH_3)_3$); ^{15}N NMR (THF): $\delta = -236.8$ (d, $^{1}J_{PN} = 78.4$ Hz), -237.9 (d, $^{1}J_{PN} = 72.5$ Hz); ^{15}N NMR(CH_2Cl_2): $\delta = -223.2$ (d, $^{1}J_{PN} = 79.7$ Hz), -223.8 (d, $^{1}J_{PN} = 74.3$ Hz); $^{31}P\{^{1}H\}$ NMR (toluene): $\delta = 148.0$; $^{31}P\{^{1}H\}$ NMR (CH_2Cl_2): $\delta = 161.5$; IR (CsI): 163 (m), 246 (w), 311 (m), 396 (m), 465 (m), 538 (s), 619 (w), 667 (w), 735 (s), 815 (s), 888 (m), 1018 (m), 1029 (w), 1084 (s), 1199 (s), 1272 (m), 1370 (m), 1400 (m), 1465 (m), 1546 (m), 1575 (m), 1687 (w), 2874 (w), 2977 (m), 3055 cm^{-1} (m); elemental analysis calcd (%) for $C_{10}H_{19}Cl_2N_2P$ (269.15): C 44.63, H 7.12, N 10.41; found C 45.02, H 7.42, N 10.51.

*Compound **3c***: Yield 97%; m.p. 137–139°C; ^{1}H NMR ($CDCl_3$): $\delta = 7.00$ (s, 2H; *m*-H); 6.90 (s, 2H; *m*-H); 6.40 (s, 1H; =CH); 2.50 (s, 6H; *o*-CH_3); 2.40 (s, 3H; *p*-CH_3); 2.38 (s, 6H; *o*-CH_3); 2.30 (s, 3H; *p*-CH_3); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): $\delta = 139.2$ (d, $^{3}J_{PC} = 2.3$ Hz; *o*-C), 138.7 (d, $^{5}J_{PC} = 4.2$ Hz; *p*-C), 138.3 (d, $^{3}J_{PC} = 2.3$ Hz; *o*-C), 136.7 (d, $^{5}J_{PC} = 7.3$ Hz; *p*-C), 134.7 (d, $^{2}J_{PC} = 9.6$ Hz; *i*-C), 131.9 (d, $^{2}J_{PC} = 10.4$ Hz; *i*-C), 130.6 (s; *m*-C), 119.1 (d, $^{2}J_{PC} = 11.4$ Hz; =CCl), 116.7 (d, $^{2}J_{PC} = 7.3$ Hz; =CH), 21.3 (s; *p*-CH_3), 21.2 (s; *p*-CH_3), 19.6 (d, $^{4}J_{PC} = 3.1$ Hz; *o*-CH_3), 19.5 (d, $^{4}J_{PC} = 1.5$ Hz; *o*-CH_3); $^{31}P\{^{1}H\}$ NMR (toluene): $\delta = 143.3$; $^{31}P\{^{1}H\}$ NMR (CH_2Cl_2): $\delta = 147.4$; IR (CsI): 162 (w), 205 (w), 239 (m), 299 (s), 389 (m), 430 (m), 452 (m), 468 (m), 505 (m), 566 (s), 587 (m), 704 (w), 745 (m), 859 (s), 942 (m), 975 (m), 1035 (m), 1132 (m), 1151 (m), 1162 (m), 1178 (m) 1223 (m), 1284 (m), 1316 (m), 1378 (m), 1480 (s), 1608 (m), 2920 (m), 3113 cm^{-1} (m); elemental analysis calcd (%) for $C_{20}H_{19}Cl_2N_2P$ (389.26): C 61.08, H 5.89, N 7.12; found C 60.88, H 6.05, N 7.11.

2-Bromo-1,3-di-*tert*-butyl-1,3,2-diazaphospholene (5a): Me_3SiBr (1.53 g, 10 mmol) was added dropwise to a cooled (0 °C) solution of **1a** (2.35 g, 10 mmol) in CH_2Cl_2. After stirring the solution for 2 h at RT, volatiles were removed in vacuo, and the residue dissolved in CH_2Cl_2/toluene (1:4). Storing the solution at −20 °C produced pale yellow crystals that were collected by filtration and dried in vacuo to give **5a** (1.6 g, 57%). M.p. 87 °C; ^{1}H NMR ($CDCl_3$): $\delta = 7.27$ (s, 2H; =CH), 1.68 (s, 18H; $C(CH_3)_3$); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): $\delta = 125.1$ (d, $^{2}J_{PC} = 7.3$ Hz; =CH), 59.8 (d, $^{2}J_{PC} = 7.6$; $C(CH_3)_3$), 30.6 (d, $^{3}J_{PC} = 9.9$ Hz; $C(CH_3)_3$); $^{31}P\{^{1}H\}$ NMR (CH_2Cl_2): $\delta = 185.2$; $^{31}P\{^{1}H\}$ NMR (toluene): $\delta = 179.9$; MS (20 eV, EI): m/z (%): 279 (2)

$[M]^+$, 199 (41) $[M-\mathrm{Br}]^+$, 143(16) $[M-\mathrm{Br}-\mathrm{C_4H_8}]^+$, 87 (100) $[M-\mathrm{Br}-2\,\mathrm{C_4H_8}]^+$; IR (CsI): 300 (w), 393 (m), 544 (s), 708 (m), 788 (s), 1024 (w), 1042 (w), 1079 (s), 1194 (s), 1234 (m), 1266 (w), 1370 (m), 1402 (m), 1468 (m), 1552 (m), 2976 (m), 3060 cm^{-1} (m); Raman: 126, 176, 254, 709, 791, 1009, 1062, 1183, 1551, 2909, 2978, 3058 cm^{-1}; elemental analysis calcd (%) for $\mathrm{C_{10}H_{20}BrN_2P}$ (279.16): C 43.03, H 7.22, N 10.03; found C 43.75 H 6.87 N 9.67.

1,3-Di-*tert*-butyl-2-fluoro-1,3,2-diazaphospholene (6a): A solution of **1a** (2.21 g, 9.4 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL) was added to solid AgF (1.19 g, 9.4 mmol), and the resulting suspension was stirred for 8 d under exclusion of light. The solvent was then removed in vacuo, and the residue suspended in hexane. The resulting mixture was filtered over Celite, and the solvent removed under reduced pressure (20 mbar). Vacuum sublimation of the residue (50 °C, 10^{-2} mbar) produced **6a** (0.48 g, 23%). M.p. 28–30 °C; ^{1}H NMR ($\mathrm{C_6D_6}$): $\delta = 6.02$ (d, $^4J_{\mathrm{FH}} = 1.8$ Hz, 2H; =CH), 1.31 (d, $^5J_{\mathrm{FH}} = 1.5$ Hz, 18H; $\mathrm{C(CH_3)_3}$); ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$): $\delta = 110.7$ (d, $^1J_{\mathrm{PF}} = 1070$ Hz); ^{31}P{^{1}H} NMR ($\mathrm{CH_2Cl_2}$): $\delta = 111.2$ (d, $^1J_{\mathrm{PF}} = 1070$ Hz); ^{19}F NMR ($\mathrm{C_6D_6}$): $\delta = -33.6$ (d, $^1J_{\mathrm{PF}} = 1066$ Hz); ^{15}N NMR ($\mathrm{C_6D_6}$): $\delta = -246.2$ (dd, $^1J_{\mathrm{PN}} = 70.1$ Hz, $^2J_{\mathrm{FN}} = 25.7$ Hz); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): $\delta = 113.0$ (dd, $^2J_{\mathrm{PC}} = 9.5$ Hz, $^3J_{\mathrm{FC}} = 2.3$ Hz; =CH), 53.5 (dd, $^2J_{\mathrm{PC}} = 13.2$ Hz, $^3J_{\mathrm{FC}} = 3.2$ Hz; $\mathrm{C(CH_3)_3}$), 31.5 (dd, $^3J_{\mathrm{PC}} = 11.1$ Hz, $^4J_{\mathrm{FC}} = 2.7$ Hz; $\mathrm{C(CH_3)_3}$); MS (16 eV, EI): m/z (%): 218 (56) $[M]^+$, 199 (3) $[M-\mathrm{F}]^+$, 162 (23) $[M-\mathrm{C_4H_8}]^+$, 106 (100) $[M-2\,\mathrm{C_4H_8}]^+$; IR (CsI): 255 (w), 401 (w), 458 (w), 508 (m), 533 (m), 600 (s), 670 (m), 706 (m) 770 (m), 820 (m), 1085 (m), 1126 (m), 1218 (m), 1280 (m), 1371 (m), 1400 (w), 1470 (w), 1597 (w), 1625 (m), 2978 (m), 3125 cm^{-1} (w); calcd for $\mathrm{C_{10}H_{20}FN_2P}$ (218.25) C 55.03, H 9.24, N 12.84; found C 53.99, H 9.02 N, 12.24.

1,3-Di-*tert*-butyl-1,3,2-diazaphospholenium tetrafluoroborate (2a[BF$_4$]): $\mathrm{AgBF_4}$ (2.92 g, 15 mmol) was added to a solution of **1a** (2.35 g, 10 mmol) in $\mathrm{CH_2Cl_2}$ (50 mL), and the resulting suspension was stirred for 1 d under exclusion of light. The suspension was filtered over celite, and the filtrate evaporated to dryness. The residue was dissolved in $\mathrm{CH_2Cl_2}$ (10 mL) and layered with hexane (50 mL). The formed light yellow crystalline precipitate was collected by filtration to give **2a**[BF$_4$] (0.8 g, 28%). M.p. 167–170 °C; ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 8.17$ (s, 2H; =CH), 1.69 (d, $^4J_{\mathrm{PH}} = 1.8$ Hz, 18H; $\mathrm{C(CH_3)_3}$]; ^{31}P{^{1}H} NMR ($\mathrm{CH_2Cl_2}$): $\delta = 202.0$; Raman: 235, 442, 703, 996, 1046, 1527, 2918, 2988, 3123 cm^{-1}.

Preparation of 1,3,2-diazaphospholenium triflates: Trimethylsilyl triflate (6.67 g, 30 mmol) was added to a cooled (0 °C) solution of the appropriate 2-chlorodiazaphospholene (10 mmol) in $\mathrm{CH_2Cl_2}$ (50 mL). The solution was allowed to warm to ambient temperature and stirred for 1 h; volatiles were then evaporated in vacuo. To remove excess trimethylsilyl triflate, the residue was triturated three times in diethyl ether, and evaporated to dryness. The residue was then dissolved in $\mathrm{CH_2Cl_2}$ (20 mL) and layered with hexane (100 mL). The formed light yellow crystalline precipitate was collected by filtration.

1,3-Dimesityl-1,3,2-diazaphospholenium triflate (2c[OTf]): Yield 4.4 g (94%); m.p. 163–166 °C; ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 8.24$ (s, 2H; =CH), 7.07 (s, 4H; *m*-CH), 2.35 (s, 6H; *p*-CH$_3$), 2.15 (s, 12H; *o*-CH$_3$); ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$): $\delta = 141.8$ (d, $^5J_{\mathrm{PC}} = 1.5$ Hz; *p*-C), 139.1 (d, $^2J_{\mathrm{PC}} = 1.9$ Hz; *i*-C), 133.9 (d, $^3J_{\mathrm{PC}} = 3.4$ Hz; *o*-C), 131.5 (d, $^2J_{\mathrm{PC}} = 6.9$ Hz; =CH), 130.5 (s; *m*-C), 21.3 (s; *p*-CH$_3$), 17.6 (s; *o*-CH$_3$); ^{31}P{^{1}H} NMR ($\mathrm{CH_2Cl_2}$): $\delta = 203.\ 3$.

1,3-Di-*tert*-butyl-4-chloro-1,3,2-diazaphospholenium triflate (7a[OTf]): Yield 3.3 g (86%); m.p. 143–145 °C; ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 7.94$ (s, 1H; =CH), 1.91 (d, $^4J_{\mathrm{PH}} = 2.6$ Hz, 9H; $\mathrm{C(CH_3)_3}$), 1.75 (d, $^4J_{\mathrm{PH}} = 2.0$ Hz, 9H; $\mathrm{C(CH_3)_3}$); ^{31}P{^{1}H} NMR ($\mathrm{CH_2Cl_2}$): $\delta = 205.\ 5$.

4-Chloro-1,3-dimesityl-1,3,2-diazaphospholenium triflate (7c[OTf]): Yield 4.2 g (84%); m.p. 152–154 °C; ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 8.10$ (s, 1H; =CH), 7.10, (s, 2H; *m*-H), 7.00 (s, 2H; *m*-H), 2.40 (s, 3H; *p*-CH$_3$), 2.30 (s, 3H; *p*-CH$_3$), 2.20 (s, 6H; *o*-CH$_3$), 2.10 (s, 3H; *o*-CH$_3$); ^{31}P{^{1}H} NMR ($\mathrm{CH_2Cl_2}$): $\delta = 205.\ 5$.

Titrations of diazaphospholenes and diazaphospholenium triflates with DBN: A solution of DBN (1.00 mol L^{-1} in $\mathrm{CH_2Cl_2}$) was added in portions of 500 µL by means of a motor burette to 50.0 mL of a solution (0.10 mol L^{-1} in $\mathrm{CH_2Cl_2}$) of the appropriate diazaphospholene compound. The mixture was stirred for 1 min after each addition, and a 500 µL sample was then transferred to an NMR tube with a calibrated microsyringe. In this manner, 20–24 samples were collected for each reaction. ^{1}H NMR spectroscopic analysis revealed that all samples displayed a single set of averaged signals for the "free" diazaphospholene and its DBN complex. The shift of signal positions during the titration indicated that both reactants are in rapid dynamic exchange and the observed chemical shift δ_{obs} may be written as Equation (4), in which δ(free), δ(cmplx) denote the chemical shifts of the "free" diazaphospholene and its Lewis base complex, respectively, χ(cmplx) the molar fraction of the complex, and c^0 the diazaphospholene concentration at the beginning of the titration.

$$\delta_{\mathrm{obs}} = \delta(\mathrm{cmplx})\,\chi(\mathrm{cmplx})\,c^0 + \delta(\mathrm{free})\,[1-\chi(\mathrm{cmplx})]\,c^0 \qquad (4)$$

The molar fraction χ(cmplx) is expressed as a function of the equilibrium constants K_1 and K_2 by solving algebraically the appropriate equations [Eqs. (1)–(3)] under consideration of the constraints imposed by charge and mass balance, yielding $\chi^1 = \{K_1(1-\tau) - [(K_1 + 4\tau - 2K_1\tau + K_1\tau^2)K_1]^{1/2}\}/[2(K_1-1)]$ for the reaction in Equation (1) and $\chi^2 = \{1 + K_2c^0(1+\tau) - \{[K_2c^0(1-\tau)-1]^2 - 4(K_2c^0)^2\tau\}^{1/2}\}/(2K_2c^0)$ for the reaction in Equation (2), in which τ denotes the degree of titration. Substitution of these terms into Equation (4) yields an expression of the form $\delta_{\mathrm{obs}} = f(\tau)$, which may serve as a target function to determine the unknown parameters K_1, K_2, δ(cmplx), and δ(free) from a fit of the experimental data in a plot of δobs versus τ. As the largest signal shifts were observed for the olefinic and aromatic protons at the diazaphospholene ring and (where applicable) mesityl substituents, we used these signals for the evaluation of the equilibrium constants K_1 and K_2. The fit of the observed values $\delta_{\mathrm{obs}}(\tau)$ to the given theoretical expression was performed by an iterative procedure with an appropriate computer program. A comparison of the experimentally observed values of δ_{obs} and the resulting best fit is displayed for **3b**/**7b** in Figure 5, and the complete set of computed equilibrium constants is given in Table 5.

Crystal structure determinations of compounds 1a, 1c, 2a[BF$_4$], 6a, 7a[OTf], and 7c[OTf]: The data were collected on a Nonius KappaCCD diffractometer at −150 °C with Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-97)[48]. The non-hydrogen atoms were refined anisotropically, H atoms were refined using a riding model (full-matrix least-squares refinement on F^2 (SHELXL-97)[49]. In **6a**, the absolute structure was determined by refining the Flack parameter,[50] and in **2a**[BF$_4$] the $\mathrm{BF_4}^-$ ion is disordered. Details of data collection and refinement are given in Table 6.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-136861 (**1a**), CCDC-136862 (**1c**), CCDC-136863 (**2a**[BF$_4$]), CCDC-136864 (**6a**), CCDC-136865 (**7a**[OTf]) and CCDC-136866 (**7c**[OTf]). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Computational studies: DFT calculations (B3LYP) were carried out using the Gaussian 98 program package[51] with a 6-31g* basis set, which was augmented by one diffuse function for all ring atoms and the exocyclic halogen atoms (6-31(+)g*). Harmonic vibrational frequencies and zero-point vibrational energies (ZPE) were calculated at the same level. All structures reported here are minima on the potential energy surface (only positive eigenvalues of the Hessian matrix). Population analyses were carried out with the NBO module[36] included in the Gaussian 98 package. A comprehensive listing of results is included in the Supporting Information.

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Table 6. Crystallographic data, and structure solution and refinement of **1a**, **1c**, **2a**[BF_4], **6a**, **7a**, and **7c**.

	1a	**1c**	**2a**[BF_4]	**6a**	**7a**[OTf]	**7c**[OTf]
formula	$C_{10}H_{20}N_2ClP$	$C_{20}H_{24}N_2ClP$	$[C_{10}H_{20}N_2P]^+[BF_4]^-$	$C_{10}H_{20}FN_2P$	$[C_{10}H_{19}N_2ClP]^+[CF_3SO_3]^-$	$[C_{20}H_{23}N_2ClP]^+[CF_3SO_3]^-$
M_r	234.7	358.8	286.1	218.3	382.8	506.9
crystal size [mm]	0.60 × 0.60 × 0.60	0.15 × 0.20 × 0.40	0.20 × 0.40 × 0.50	0.10 × 0.20 × 0.30	0.10 × 0.35 × 0.45	0.10 × 0.30 × 0.40
crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic	triclinic
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$Pna2_1$ (No. 33)	$Pbca$ (No. 61)	$P\bar{1}$ (No.2)
a [Å]	10.6873(2)	7.5153(2)	7.2810(2)	9.5595(8)	11.9542(6)	10.2625(8)
b [Å]	9.3466(1)	29.1919(5)	13.9886(3)	11.7404(13)	11.7785(6)	10.8096(9)
c [Å]	12.8645(2)	8.5586(2)	14.1699(4)	10.9883(11)	24.1326(10)	12.5458(9)
α [°]						98.956(4)
β [°]	99.108(1)	94.808(1)	97.537(1)			106.243(4)
γ [°]						114.600(3)
V [Å^3]	1268.83(3)	1871.03(7)	1430.75(6)	1233.2(2)	3397.9(3)	1154.4(2)
Z	4	4	4	4	8	2
ρ [g cm^{-3}]	1.23	1.27	1.33	1.18	1.50	1.46
μ [mm^{-1}]	0.40	0.29	0.22	0.20	0.48	0.38
F(000)	504	760	600	472	1584	524
T [K]	123(2)	123(2)	123(2)	123(2)	123(2)	123(2)
$2\theta_{max}$ [°]	56.6	56.7	56.6	59.8	56.5	56.6
index range	$-14 \leq h \leq 14$	$-10 \leq h \leq 10$	$-9 \leq h \leq 9$	$-12 \leq h \leq 8$	$-15 \leq h \leq 15$	$-13 \leq h \leq 13$
	$-12 \leq k \leq 12$	$-38 \leq k \leq 37$	$-18 \leq k \leq 17$	$-11 \leq k \leq 16$	$-13 \leq k \leq 13$	$-12 \leq k \leq 12$
	$-17 \leq l \leq 17$	$-11 \leq l \leq 11$	$-18 \leq l \leq 18$	$-14 \leq l \leq 10$	$-32 \leq l \leq 32$	$-15 \leq l \leq 15$
reflections measured	32101	25848	20277	6503	23673	16129
unique reflections	3113	4570	3487	2649	3194	4240
observed reflections [$I > 2\sigma(I)$]	2941	3853	2806	2114	2446	3178
R_{int}	0.035	0.33	0.032	0.038	0.048	0.036
parameters/restraints	127/0	223/0	200/310	127/1	199/0	295/0
R [$I > 2\sigma(I)$]	0.026	0.032	0.041	0.042	0.038	0.034
$wR2$ (all data)	0.067	0.090	0.129	0.097	0.110	0.094
Flack parameter				0.1(1)		
difference peak max/min [e Å^{-3}]	−0.27/0.32	−0.39/0.31	−0.37/0.33	−0.32/0.75	−0.51/0.29	−0.42/0.25

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