Cation Stabilities, Electrophilicities, and "Carbene Analogue" Character of Low Coordinate Phosphorus Cations

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The stabilities of low coordinated phosphorus cations can be expressed in the frame of the HSAB concept by the transferred charge density $\Delta q(N)$ which a cation receives upon formation of a donor-acceptor adduct with a Lewis base N. This concept allows to differentiate between relative stabilities towards different reaction partners, and to compare the electrophilicities of phosphenium ions to those of isoelectronic carbenes and silylenes. An analysis of substituent influences on $\Delta q(H)$ in cations $[P(R)_2]^+$ suggests an increasing stabilizing power of substituents in the series $R = Cl < CH_3 < OH, SH < NH_2$. The same ordering was derived from isodesmic hydride transfer reactions. Interpretation of population analyses suggests that the individual substituent contributions to cation stabilities result from a balance between π-donation into the empty p(P) orbital and electrostatic stabilization by polar P–R σ-bonds. A further stabilizing effect, which is of similar magnitude as in isoelectronic carbenes or silylenes, may arise from cyclic π-conjugation between a diaminophosphenium fragment and an adjacent double bond. Substituent effects influence further the nature of the frontier orbitals of phosphenium ions, resulting in orbital sequences which resemble those of carbenes, allyl anions, or phospholides, respectively. The absence of frontier orbital related changes in reactivity patterns suggests that in all reactions, including metal complex formation, phosphenium ions behave as purely *electrophilic* rather than *ambiphilic* species.

Introduction

Belonging to the first isolable compounds with (p-p)π bonding to phosphorus, amino-phosphenium ions, $[P(NR_2)(R')]^+$, and phosphanetriyl-ammonium ions, $[P\equiv N-R]^+$, have received continuous attention during the last 25 years and are still objects of current interest.[1] The results of extensive studies of chemical reactivities have coined the opinion that the cations are ambiphiles which have both nucleophilic and electrophilic properties. The electrophilic character comes to the fore in C–H- and C–C bond insertion reactions, cycloadditions, and complex formation with Lewis bases, while the nucleophilic properties are considered responsible for the formation of transition metal complexes.[1]

In contrast to the wealth of experimental studies, theoretical investigations of these cations are rare. Earlier ab-initio calculations on simple model systems ($[P(H)_2]^+$, $[P(H)(NH_2)]^+$, $[P(NH_2)_2]^+$) confirmed singlet ground states and revealed the stabilizing effect of conjugation between nitrogen lone-pairs and the empty p-orbital at phosphorus which resulted in a heteroallylic frontier orbital sequence for $[P(NH_2)_2]^+$.[1a][2] For selected cyclic cations, the issue of conjugation between amino(thioxo)phosphenium fragments and adjacent double bond systems to form "aromatic" π-systems was discussed.[3] Only recently, Schoeller et al. reported a first attempt to establish a relative scale of gas phase stabilities for selected cations from a comparison of

hydride transfer reaction energies.[4] In addition, a discussion of molecular structures and frontier orbitals was presented which substantiated the isolobal relationship between phosphenium ions and carbenes, and between phosphanetriyl-ammonium ions (and the isoelectronic PO$^+$ and PS$^+$ cations) and (iso)cyanides.
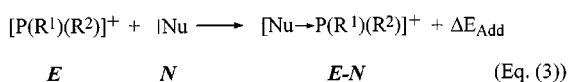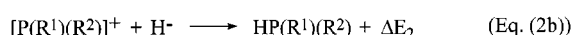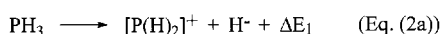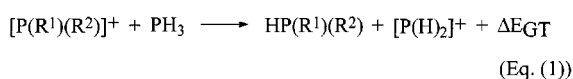
Regarding that low coordinate phosphorus cations engage frequently in donor-acceptor interactions with nucleophilic counter ions or solvents,[1c] it becomes clear that in condensed phases their stability and electrophilicity are closely connected. It is the primary objective of this work to attempt an analysis of cation stabilities which not only covers a wider range of molecular structures, but also takes this effect explicitly into consideration. For this purpose, a concept is proposed which is based on a discussion of stability and electrophilicity in the frame of the extended HSAB concept.[5][6] The pivotal idea is to use the amount of charge transfer which a cation receives in the formation of a donor-acceptor adduct as a measure of its stability. In order to elucidate the origin of the stability differences, a discussion of population analyses is presented which suggests an interplay between mesomeric effects and electrostatic contributions associated with high P–R bond polarities. To highlight further the connection between electronic structure and reactivity, some comments on frontier orbital sequences and the "carbenic" nature of phosphenium ions will be made.

Results and Discussion

Stability and Electrophilicity of Low Coordinate Phosphorus Cations

Relative gas phase stabilities of phosphenium ions $[P(R^1)(R^2)]^+$ can be determined according to Schoeller et al. by comparing the energies ΔE_{GT} of the hydride transfer reaction of Eq. (1) (Scheme 1).[4] Formally, this reaction can be separated into two steps as described by Eq. (2a) and (2b). Since Eq. (2a) and ΔE_1 remain the same for different cations, ΔE_{GT} essentially quantifies the variation in hydride affinities, ΔE_2. In view of the fact that the stability of phosphenium ions in condensed phases is often limited by their tendency to form Lewis acid-base adducts with solvent molecules or counter ions [Eq. (3)],[1] of which the reaction with a hydride is just a special case, Schoeller's definition may easily be put in a more general form: relative stabilities of cations E (in condensed phases) are reflected in different energies ΔE_{Add} associated with the formation of covalent donor-acceptor adducts $E-N$ with a given nucleophile N (counter ion or solvent).

Scheme 1

$$[P(R^1)(R^2)]^+ + PH_3 \longrightarrow HP(R^1)(R^2) + [P(H)_2]^+ + \Delta E_{GT}$$

(Eq. (1))

$$PH_3 \longrightarrow [P(H)_2]^+ + H^- + \Delta E_1 \quad \text{(Eq. (2a))}$$

$$[P(R^1)(R^2)]^+ + H^- \longrightarrow HP(R^1)(R^2) + \Delta E_2 \quad \text{(Eq. (2b))}$$

$$[P(R^1)(R^2)]^+ + |Nu \longrightarrow [Nu{\rightarrow}P(R^1)(R^2)]^+ + \Delta E_{Add}$$

$$E \qquad\quad N \qquad\qquad E\text{-}N \qquad\qquad \text{(Eq. (3))}$$

On a first glance, this approach seems to offer no obvious advantage, since a concise evaluation of hydride or nucleophile affinities imposes more severe computational problems than calculation of the energies of isodesmic hydride transfer reactions.[7] However, as an estimation of *relative* stabilities requires only the correct evaluation of trends in adduct formation energies ΔE_{Add} rather than their true values, an approximate solution to the problem can be obtained on a much simpler level.

Thus, the formation of a donor–acceptor bond in the adduct $E-N$ [Eq. (3)] induces a charge transfer $\Delta q(N)$ from N to the phosphorus cation. Using the principle of electronegativity equalization,[5][8] $\Delta q(N)$ can be approximated as $\Delta q(N) = (\chi^e - \chi^n)/(\eta^e + \eta^n)$. Here, $\chi^{e(n)}$ and $\eta^{e(n)}$ denote the absolute electronegativity and absolute hardness of the cation (nucleophile), whose operational definitions are $\chi = -(I + E)/2$ and $\eta = (E - I)/2$ (I = ionization potential, E = electron affinity) in the frame of the extended HSAB concept.[5] Within Hartree-Fock theory, χ and η may be approximated as $\chi = -(\varepsilon_{HOMO} + \varepsilon_{LUMO})/2$ and $\eta = (\varepsilon_{LUMO} - \varepsilon_{HOMO})/2$ by using Koopman's theorem.[6] It may be noted that, despite the severe deficiencies of this
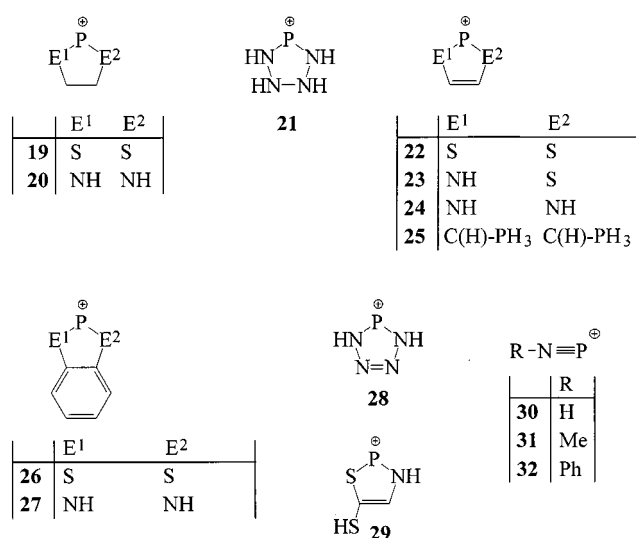
approximation,[9][10] qualitative trends in χ and η between related molecules are reproduced at this level with sufficient accuracy.[10][11]

If we compare the interactions of two cations with an arbitrary nucleophile (e.g. $N = H^-$), the less stable cation will receive a larger charge transfer and form a stronger bond. Presuming a monotonous relation between the transferred charge density $\Delta q(N)$ and the donor–acceptor bond strength ΔE_{Add},[12] an increase in $\Delta q(N)$ corresponds to an increase in ΔE_{Add} and thus a lower cation stability, and vice versa, so that $\Delta q(N)$ values can in principle be used directly as indicators of relative stabilities.

In order to apply this concept we computed transferred charge densities $\Delta q(H)$ for some 30 model cations with low coordinate phosphorus atoms, using hydride as an archetypal nucleophile. The studied systems (Scheme 2) include cyclic and acyclic phosphenium ions $[P(R^1)(R^2)]^+$ (R^1, R^2 = H, Ph, Cl, alkyl, alkoxy, thioxo, amino), the 1.3-bisphosphanyl-phosphapropenides and -phospholides **12**, **25** which are isolobal and isoelectronic to the diaminophosphenium ions **11**, **24**,[13] and the phosphanetriyl-ammonium ions **30−32**. Details on the calculations are given in the experimental section; the resulting values of $\Delta q(H)$ are listed in Table 1, together with frontier orbital energies and the values of χ and η.

Scheme 2. (* = Ph-group orientation parallel (**17**) and orthogonal (**17′**) with respect to $P-NH_2-$plane)

	R¹	R²		R¹	R²		R¹	R²
1	H	H	**7**	Cl	Cl	**13**	Cl	NH₂
2	H	Me	**8**	Me	Me	**14**	Me	NH₂
3	H	Cl	**9**	OH	OH	**15**	OH	NH₂
4	H	OH	**10**	SH	SH	**16**	SH	NH₂
5	H	SH	**11**	NH₂	NH₂	**17,17′ ***	Ph	NH₂
6	H	NH₂	**12**	C(H)-PH₃	C(H)-PH₃	**18**	NMe₂	NMe₂

	E¹	E²
19	S	S
20	NH	NH

21

	E¹	E²
22	S	S
23	NH	S
24	NH	NH
25	C(H)-PH₃	C(H)-PH₃

	E¹	E²
26	S	S
27	NH	NH

28

29

	R
30	H
31	Me
32	Ph

Inspection of the computed $\Delta q(H)$ values reveals an increasing stabilizing effect of the substituents R^1, R^2 in a

Table 1. Frontier orbital energies, absolute electronegativities and hardness, transferred charge densities Δq(H), and cation stabilization energies ΔE_{GT} at MP2/6-31+g(d) level for **1−32**

[a]	ε_{HOMO} [eV]	[b]	ε_{LUMO} [eV]	[b]	χ [eV]	η [eV]	Δq(H) [c]	ΔE_{GT} [kcal/mol]
1 (C_{2v})	−19.79	a_1(n)	−8.56	b_1(p*)	14.17	5.62	1.08	0.0
2 (C_s)	−18.30	a′(n)	−7.40	a″(π*)	12.85	5.45	0.99	−22.2
3 (C_s)	−18.57	a′(n)	−8.04	a″(π*)	13.30	5.26	1.04	−18.9
4 (C_s)	−19.08	a′(n)	−7.18	a″(π*)	13.13	5.95	0.97	−39.5
5 (C_s)	−18.13	a′(n)	−7.11	a″(π*)	12.62	5.51	0.96	−45.6
6 (C_s)	−18.69	a′(n)	−6.11	a″(π*)	12.40	6.29	0.89	−66.3
7 (C_{2v})	−18.60	a_1(n)	−7.71	b_1(π*)	13.15	5.45	1.01	−32.8
8 (C_s)	−17.20	a′(n)	−6.50	a″(π*)	11.82	5.39	0.91	−40.6
9 (C_{2v})	−19.46	a_1(n)	−5.99	b_1(π*)	12.72	6.74	0.89	−63.3
10 (C_{2v})	−16.36	a_2(π_2)	−6.38	b_1(π*)	11.37	4.99	0.90	−62.3
11 (C_{2v})	−17.63	a_2(π_2)	−4.40	b_1(π*)	11.02	6.62	0.77	−93.8
12 (C_{2v})	−12.05	a_2(π_2)	−2.17	b_1(π*)	7.11	4.94	0.54	−145.7
13 (C_s)	−18.32	a′(n)	−6.00	a″(π*)	12.16	6.16	0.88	−63.9
14 (C_s)	−17.50	a′(n)	−5.41	a″(π*)	11.45	6.05	0.83	−77.3
15 (C_s)	−18.90	a′(n)	−5.18	a″(π*)	12.04	6.86	0.83	−80.2
16 (C_s)	−16.67	a″(π_2)	−5.44	a″(π*)	11.06	5.61	0.83	−76.7
17 (C_s)	−13.76	a″(π_2)	−4.77	a″(π*)	9.27	4.49	0.76	−97.2
17′ (C_s)	−13.42	a″(π_2)	−4.98	a″(π*)	9.20	4.22	0.77	−86.3
18 (C_2)	−14.80	a(π_2)	−3.60	b(π*)	9.20	5.60	0.68	−107.5
19 (C_2)	−15.50	a(π_2)	−5.85	b(π*)	10.67	4.82	0.85	−76.9
20 (C_2)	−15.85	a(π_2)	−4.15	b(π*)	10.00	5.85	0.73	−107.9
21 (C_2)	−16.25	a(π_2)	−4.91	b(π*)	10.58	5.67	0.79	−85.7
22 (C_{2v})	−15.07	b_1(π_3)	−5.82	b_1(π*)	10.44	4.62	0.85	−90.8
23 (C_s)	−14.59	a″(π_3)	−5.07	a″(π*)	9.83	4.76	0.79	−107.9
24 (C_{2v})	−14.10	b_1(π_3)	−4.17	b_1(π*)	9.13	4.97	0.71	−129.0
25 (C_{2v})	−11.31	b_1(π_3)	−1.85	b_1(π*)	6.58	4.73	0.51	−173.1
26 (C_{2v})	−13.52	b_1(π_3)	−5.52	b_1(π*)	9.52	4.00	0.81	−86.9
27 (C_{2v})	−12.90	b_1(π_3)	−4.24	b_1(π*)	8.57	4.33	0.70	−120.9
28 (C_{2v})	−17.09	b_1(π_3)	−5.39	b_1(π*)	11.24	5.85	0.83	−97.3
29 (C_s)	−14.15	a″(π_3)	−5.41	a″(π*)	9.78	4.37	0.81	−94.8
30 ($C_{\infty v}$)	−20.37		−6.09		13.23	7.14	0.90	−78.3
31 (C_{3v})	−18.47		−5.42		11.94	6.52	0.84	−94.8
32 (C_{2v})	−13.26		−5.13		9.20	4.06	0.78	−99.5

[a] Symbols in parentheses denote the molecular point group. − [b] Symmetry race and type of the orbital (in parentheses); n = phosphorus lone-pair, π_2 = heteroallylic π_2-orbital, π_3 = "pholide" type orbital (see text), p* = unoccupied phosphorus p-orbital, π* = π*-orbital with P−X antibonding character. − [c] Δq(H) = −[χ − χ(H)]/[η + η(H)]; values of χ(H) and η(H) taken from ref.[6]

cation $[P(R^1)(R^2)]^+$ in the series R^1, R^2 = H < Cl < Me < SH, OH < Ph < NH$_2$ < C(H)PH$_3$. A general increase in stability is further observed upon replacement of hydrogens at an adjacent element E in EH$_n$-fragments by alkyl groups, and of −CH$_2$CH$_2$− moieties in the five membered rings of cyclic cations by ethylene or phenylene units. On the whole, the order of relative stabilities of the model systems is in accord with interpretations of physical and chemical properties of experimentally known cations.[1]
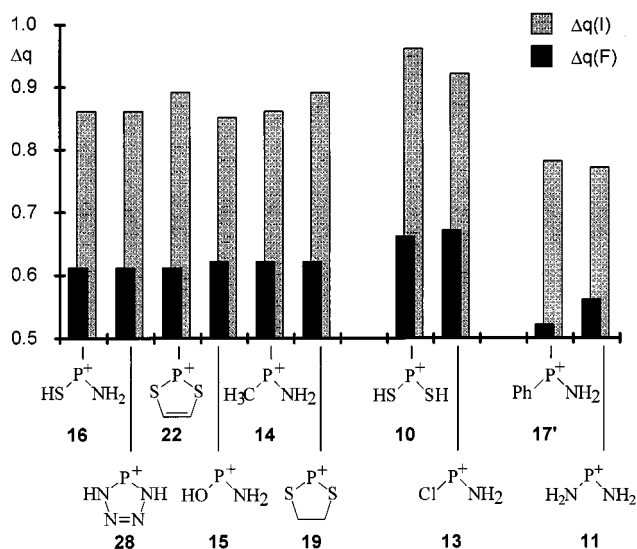
Transferred charge densities for the interaction of phosphenium ions with a variety of anionic (e.g. halides) and neutral nucleophiles (NMe$_3$, PMe$_3$) can be computed straightforwardly. The results, which are not included here for the sake of shortness, give on the whole a similar account of relative cation stabilities as Δq(H) values. A detailed inspection reveals, however, some characteristic deviations which mirror a preference for "hard-hard" or "soft-soft" over "hard-soft" interactions in the sense of the HSAB concept.[5] Some examples involving the interaction of selected phosphenium ions with a hard (F$^−$) and soft nucleophile (I$^−$) are illustrated in Scheme 3. Thus, the similarity of Δq(F) for **14−16**, **19**, **22**, **28** suggests nearly identical stabilities towards F$^−$, whereas towards I$^−$, the softer cations with sulfur substituents receive a larger charge transfer Δq(I) (and are hence considered less stable) than

cations with oxygen or nitrogen substituents. Still more pronounced variations are noted for **10**, **13** and **11**, **17′**, which display a reversed order of relative stabilities depending on whether the interaction of the cations with F$^−$ or I$^−$ is considered.
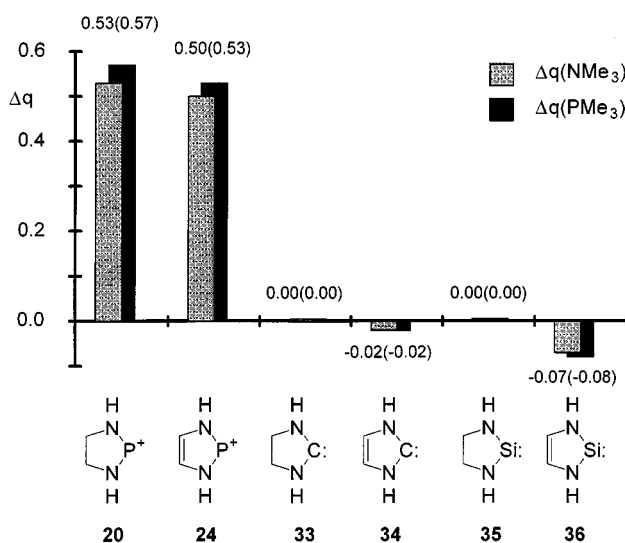
Extension of the concept to other species than phosphenium ions should further allow to compare the Lewis acid/base behavior of different types of electrophiles. As an example, the interaction of trimethylamine and -phosphane with cyclic diaminophosphenium ions and isoelectronic carbenes and silylenes was considered, (Scheme 4). The magnitude of Δq for the cations **22**, **24** reflects their electrophilicity and is in accord with the known tendency of phosphenium ions to form stable donor adducts.[1] In contrast, Δq values for the carbenes and silylenes **33−36** are close to zero, or even negative,[14] indicating that the electrophilic character is negligible. This is in line with experimental evidence for low π-acceptor capabilities and classification of these systems as *nucleophilic* carbenes (silylenes).[1c][15]

In order to compare relative stabilities derived from transferred charge densities with hydride transfer energies, we have also computed stabilization energies ΔE_{GT} for **1−32** at the MP2/6-31+g(d) level. The results are included in Table 1. According to a regression analysis, ΔE_{GT} and Δq(H) are connected by a linear relation (correlation coef-

Scheme 3. Comparison of transferred charge densities for the inter-
action of selected phosphenium ions with fluoride
[$\Delta q(F^-)$] and iodide [$\Delta q(I^-)$] anions. Values of χ and η
employed in the calculation of Δq were taken from table
1 for the cations; for the halide anions, the correspon-
ding data of the neutral atoms given in ref.[5] were used

Scheme 4. Comparison of transferred charge densities $\Delta q(NMe_3)$
and $\Delta q(PMe_3)$ for isoelectronic diaminophosphenium
cations and neutral diaminocarbenes and -silylenes. All
values of χ and η employed in the calculation of Δq
were taken from MP2/6-31+g(d) orbital energies of
MP2 optimized molecular structures

Figure 1. Plot of $\Delta q(H)$ vs. ΔE_{GT} for **1−32** (solid circles) and result
of a linear regression analysis [solid line, $\Delta q(H)_{regr} = 3.30 \cdot 10^{-3}$
$\Delta E_{GT} + 1.10$, correlation coefficient $r = 0.96$]

ners according to the HSAB concept. However, since the
pivotally important quantities χ and η are molecular and
not orbital properties, the origin of the stability differences
remains obscure. In order to obtain further insight in the
bonding situation of low coordinate phosphorus cations, we
have attempted a more detailed analysis of the electronic
structure based on the results of natural population analy-
ses (NPA).[16]

π-Interactions vs. σ-Bond Polarization: Most discussions
on the origin of the stabilization of phosphenium ions focus
on mesomeric interactions of the formally empty p-orbital
at phosphorus with adjacent π-donors.[2][3][4] The varying
extent of this π-donation in different cations may be esti-
mated in a straightforward manner by comparing either the
electron populations in the phosphorus p-orbital, $n_\pi(P)$, or
the bond orders in the P−X bonds. A listing of the values
of $n_\pi(P)$ as well as Wiberg bond indexes[16] for the phos-
phenium ions **1−29** is given in Table 2. For the simplest
case, [P(H)$_2$]$^+$, $n_\pi(P)$ is nearly zero, indicating vanishing π-
stabilization. Introduction of ER$_n$-groups at phosphorus in-
duces partial population of the p-orbital via dative (E−P)-
π-interactions (ER$_n$ = Cl, OR, SR, NR$_2$), or hyperconjug-
ation (ER$_n$ = CR$_3$), and $n_\pi(P)$ increases in the order ER$_n$ =
CR$_3$ < OR < Cl < NR$_2$ < SR. The same order of increasing
π-stabilizing capabilities emerges also from the comparison
of Wiberg bond indexes.

Interestingly, the above mentioned ordering according to
increasing degree of E−P π-stabilization differs markedly
from the order of overall cation stabilities. Here, regardless
if one refers to a comparison of $\Delta q(N)$ or ΔE_{GT} values,
cations with NR$_2$- and OR groups should be more stable
than analogous derivatives with SR- or Cl substituents,
respectively. This discrepancy suggests that further influ-
ences beside mesomeric stabilization have a significant ef-
fect on cation stability. In order to understand the underly-
ing mechanisms, a comparison of the bonding situation in
phosphenium ions and carbenium ions of the type
[C(EH)$_3$]$^+$ (E = chalcogen) appears useful. For the latter it
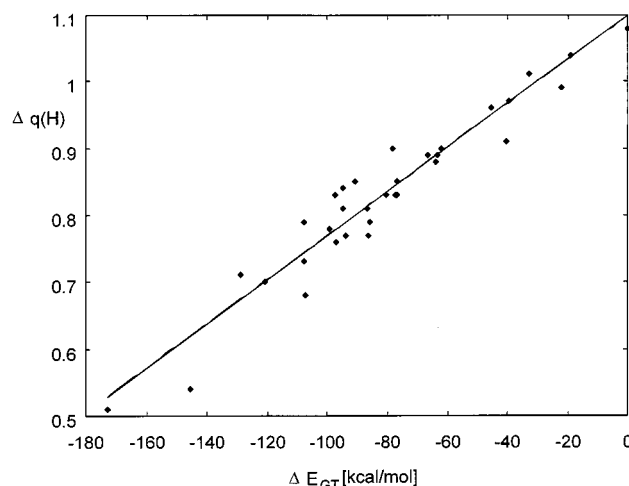
ficient $r = 0.96$, Figure 1). This suggests that despite some
discrepancies in the assessment of the stability of individual
cations, which are reflected in the scatter of the data, both
scales give a similar account of the general trends which
govern the stability of low coordinate phosphorus cations.

Electronic Origin of the Stability of Phosphenium Cations

Appealing features of the application of $\Delta q(N)$ to predict
relative stabilities (and reactivities) are the use of a mini-
mum number of parameters, and the possibility to dis-
tinguish between stabilities towards different reaction part-

Table 2. Electron population in the phosphorus p(π)-orbital [n$_\pi$(P)], "electrostatic factors" $\varepsilon = 1/2 \sum [q(P) \, q(X_i)]/[r(PX_i)]$, and P−X Wiberg bond indices for the phosphenium cations **1−29**. Natural charges $q(P, X_i)$, orbital populations n$_\pi$(P), and Wiberg bond indices were computed from NPA analyses of MP2/6-31+g* electron densities

	n$_\pi$(P)	Wiberg Indices		ε
1	0.02	P−H 0.96		−0.02
2	0.12	P−C 1.02	P−H 0.95	−0.42
3	0.37	P−Cl 1.40	P−H 0.94	0.00
4	0.31	P−O 1.08	P−H 0.94	−0.39
5	0.58	P−S 1.66	P−H 0.94	0.02
6	0.46	P−N 1.34	P−H 0.93	−0.37
7	0.55	P−Cl 1.25		−0.01
8	0.18	P−C 0.98		−0.91
9	0.42	P−O 0.94		−1.04
10	0.75	P−S 1.35		−0.01
11	0.56	P−N 1.08		−1.06
12	0.80	P−C 1.26		−0.63
13	0.57	P−Cl 1.11	P−N 1.20	−0.47
14	0.45	P−C 0.93	P−N 1.26	−0.87
15	0.51	P−O 0.87	P−N 1.16	−1.04
16	0.64	P−S 1.29	P−N 1.14	−0.40
17	0.55	P−C 1.01	P−N 1.15	−0.61
17'	0.46	P−C 0.89	P−N 1.27	−0.64
18	0.70	P−N 1.05		−0.64
19	0.78	P−S 1.32		0.06
20	0.61	P−N 1.06		−0.83
21	0.63	P−N 1.06		−0.68
22	1.04	P−S 1.21		0.08
23	0.98	P−N 0.95	P−S 1.19	−0.12
24	0.94	P−N 0.95		−0.55
25	1.06	P−C 1.10		−0.34
26	1.02	P−S 1.21		0.08
27	0.90	P−N 0.96		−0.57
28	0.78	P−N 0.99		−0.50
29	0.95	P−N 1.01		−0.09

was shown recently,[17] that beside (E−C) π-donation also the polarity of the C−E bonds may add substantially to the stabilization energy. The effect is most pronounced for E = O, where the high σ bond polarity [C$^{(+)}$−O$^{(−)}$] overcompensates the O→C-π-electron shift. This leads to a net increase of charge separation in the C−O bond and results in a marked contribution of the Coulomb-term to the bond energy.

The assessment of a similar contribution to the stability of phosphenium ions [P(E^{1}R$_n$)(E^{2}R$_n$)]$^+$ becomes feasible from a comparison of the "electrostatic factors"

$$\varepsilon = 1/2 \sum_{i=1}^{2} \frac{q(P) \, q(E^i)}{r(PE^i)}$$

which characterize the average Coulomb stabilization associated with the presence of polar P−E bonds based on a simple point-charge model. A comparison of the listed values of ε in Table 2 reveals an increasing Coulomb stabilization in the order X = S ≈ Cl << N < O. If we assume that the overall cation stability is influenced by both Coulomb and π-donor contributions (which increase with n$_\pi$(P) in the order OH < Cl < NH$_2$ < SH), the higher stabilizing power of NH$_2$- with respect to OH- (which exert stronger Coulomb stabilization) or SH-groups (which are better π-donors) is consistently explained as the consequence of a balance of both effects. Likewise, the slightly higher stabilizing effect of a CH$_3$- as compared to a Cl-substituent is attribu-

table to overcompensation of the lower π-donor capability of the former by a larger Coulomb stabilization.

A heuristic confirmation of this concept can be derived from a correlation analysis involving n$_\pi$(P), ε, and ΔE_{GT} as an indicator of overall cation stabilities. While a regression analysis between n$_\pi$(P) and ΔE_{GT} for the phosphenium ions **1−11**, **13−24**, **26−29** yielded a linear relation with a correlation coefficient $r = 0.77$, a nonlinear fit using both n$_\pi$(P) and ε as independent variables furnished the equation $E_{GT,regr} = -3(10) + 92(15) \, n_\pi(P) - 89(15) \, \varepsilon - 49(16) \, \varepsilon^2$, with a correlation coefficient $r = 0.88$. Despite the still substantial scatter of the data, it is apparent that the two parameter model gives a more concise account on phosphenium ion stabilities than the consideration of mesomeric effects alone.
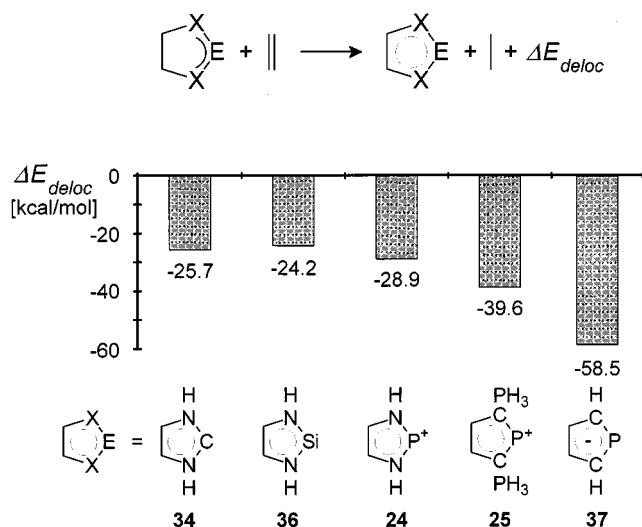
Cyclic π-Conjugation: An issue which attracted considerable interest and was debated rather controversially is the formation of delocalized 6(10)π-systems in cyclic cations such as **22−29**.[3][18][19][20] Positive evidence for the presence of conjugation of this type is provided both by the increase of n$_\pi$(P) and the decrease of Δq(H) (or increase of ΔE_{GT}, respectively) for **22 - 29** relative to their CC-saturated analogues **19−21** (cf. Table 1). The net energetic gain [e.g. $\Delta(\Delta E_{GT})$ 21.1 and 13.9 kcal/mol for **20/24** and **19/22**, respectively] is, however, much lower than the inherent mesomeric stabilization in the PE$_2$ fragment {E = N, S; $\Delta(\Delta E_{GT})$ 93.8 and 62.3 kcal/mol between [P(H)$_2$]$^+$ and [P(NH$_2$)$_2$]$^+$ or [P(SH)$_2$]$^+$}; it may rather be compared to the inductive stabilization which results from replacement of H in EH$_n$-moieties by alkyl groups {e.g. $\Delta(\Delta E_{GT})$ 13.7 kcal/mol for [P(NH$_2$)$_2$]$^+$ and [P(NMe$_2$)$_2$]$^+$}.

As we have demonstrated earlier for **25**, the energetic effects of cyclic π-conjugation may also be analyzed in terms of the reaction energy of the homodesmotic reaction of Scheme 5.[13] This approach is easily extended to a comparison of the π-electron structures in the isoelectronic carbene analogues **24**, **33**, and **35**. The value of ΔE_{deloc} in the cation **24** is higher (4−5 kcal/mol) than in **33** or **35**, but still notably lower than in **25** or the isolobal[13] phospholide anion **37** (Scheme 5). Without attempting to establish a quantitative scale, these results indicate that all three carbene analogues exhibit only weak aromatic character, even if cyclic conjugation in the cation **24** is somewhat more effective than in the neutral species **33**, **35**.[21] Natural population analyses indicate further that the increase in n$_\pi$(P) in **24** relative to **20** results from a shift of π-electron density within the N$_2$P-unit, and not from a net transfer from the C$_2$ to the N$_2$P fragment. In a simple orbital picture, this corresponds to mixing of occupied and empty N$_2$P-π orbitals under perturbation by the additional double bond.

Frontier Orbital Considerations

Phosphenium ions are with regard to their reactivity generally considered as carbene analogues.[1][2] The justification for this hypothesis was derived from the similarity of the HOMO (phosphorus lone pair) and LUMO (empty p-orbital) in [P(H)$_2$]$^+$ (Figure 2a) and the parent carbene,

Scheme 5. Isodesmic reactions describing the interaction of hete-roallylic $N_2E(C_2E)$-fragments in cyclic phosphenium ions, carbenes, silylenes, and phospholide anions with an adjacent double bond. Reaction energies ΔE_{deloc} were calculated at the MP2/6-31+g(d) + ZPE level. The value for **25** was taken from ref.[13]
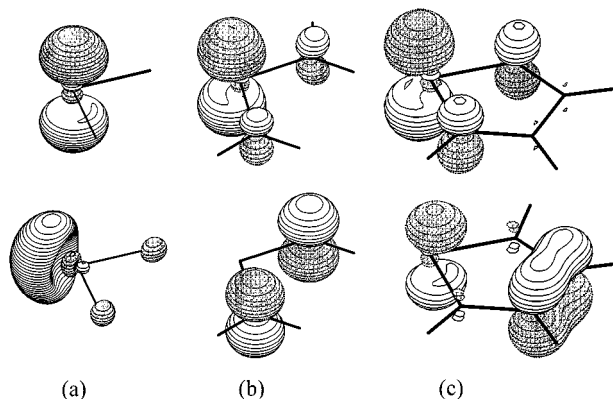

Figure 2. MOLDEN[29] plot of the LUMO (top row) and HOMO (bottom row) of (a) $[P(H)_2]^+$ (**1**), (b) $[P(NH_2)_2]^+$ (**11**), and (c) [cyclo-$P(NH_2)_2(CH)_2]^+$ (**24**). The shown surfaces correspond to electron densities of (a) 0.14, (b) 0.10, and (c) 0.09, respectively

(a)   (b)   (c)

CH_2, which makes the two systems both isolobal and iso-electronic.[1][2]

Inspection of the frontier orbitals of cations **1−29** (Table 1) reveals that this analogy is not preserved in all cases. A true carbene analogue frontier orbital sequence is confined to cations with small to moderate E→P-π stabilization such as $[P(H)(X)]^+$ (X = any substituent) or $[P(NH_2)(Y)]^+$ (Y = Cl, CH₃, OH). The frontier orbitals of cations $[P(ER_n)_2]^+$ with two strong π-donor groups (ER_n = NH₂, NMe₂, SH) resemble in accord with earlier studies[2][4] those of an allyl anion (Figure 2b): the HOMO is an antisymmetric combination of $p_\pi(E)$-orbitals with a node at phosphorus, and the LUMO an antibonding π_3^*-orbital. The "lone pair" at phosphorus corresponds to the HOMO-1 and lies 0.5−2.4 eV below the HOMO. The LUMO of the cyclic conjugated cations **22−29** is similar to the previous case, but the HOMO resembles now the highest occupied π-orbital of a phospholide anion[13] and has a large coefficient at phosphorus (Figure 2c). The highest σ-orbital with significant "lone-pair"-character lies 1.8−4.9 eV below the HOMO.

In the frame of frontier orbital theory, one can expect that such significant variations in the type of frontier orbitals imply concomitant changes in reactivity patterns. That this is actually not observed may be explained on the basis of a closer inspection of frontier orbital interactions for individual reactions. In the majority of known reactions which comprise oxidative additions and cycloadditions, phosphenium ions act as electrophiles,[1] and the dominant frontier orbital interaction involves the LUMO of the cation and the HOMO of the reaction partner. Since the largest lobe in the LUMO is always centered at the phosphorus-p-orbital, no changes in frontier orbital interactions or reactivity patterns are expected.

The most prominent reaction which supposedly reflects the nucleophilic character of phosphenium ions is the for-

mation of transition metal complexes. The phosphorus-metal bonding can in this case be described as superposition of a dative P→M σ- and a retrodative P←M π-bond.[1c][22] An analysis of frontier orbital interactions must therefore consider both the HOMO(cation)-LUMO(metal) and LU-MO(cation)-HOMO(metal) interactions, and the reactivity of the cation will be directed by the electron densities in *both* of its frontier orbitals.

For "carbene analogue" cations such as **1** where the maximum electron density in both HOMO and LUMO occurs at phosphorus, the formation of dative P→M-σ- and P←M-π-bonds is straightforward. For "heteroallylic" cat-ions such as **11**, the shapes of the frontier orbitals imply that a nucleophilic attack of the ligand at a transition metal should occur via the nitrogen,[23] and an electrophilic attack via the phosphorus. The observed formation of P-coordi-nated complexes[1] suggests therefore that the metal-ligand interaction is dominated by the LUMO(cation)-HOMO-(metal) contribution. Since the HOMO of the cation has a node at phosphorus, secondary interactions between LUMO(metal) and HOMO-1 (phosphorus lone pair) be-come important, leading to the same bonding description as before. It should be noted that, even if the results of this analysis agree with the generally acknowledged picture of phosphorus-metal bonding in phosphenium complexes[1], they suggest a different weighting of the two contributions: the dominant interaction is here the P←M π- rather than the P→M σ-contribution, and the electrophilic character of phosphenium cations commands even the reaction with transition metal substrates.[24][25]

In the cyclic cations **22−29**, the shapes of HOMO and HOMO-1 (which likewise resembles the HOMO-1 of a phospholide[13] and is very close in energy) suggest that a nucleophilic attack at a metal should favor side-on coordi-nation via the π-electron system, while for an electrophilic attack a similar situation as in the previous examples pre-vails. So far, stable complexes of diazaphospholenium ions of either type are unknown, but the preference of bis-phos-phonio-benzophospholides to form σ-complexes[1c] suggests

that the coordination properties may still reflect the electrophilic character of these cations.[26]

Conclusions

The results of the presented studies may be summarized as follows:

(1) Transferred charge densities $\Delta q(N)$, which describe the shift of electron density upon formation of a dative bond between a low coordinate phosphorus cation and a nucleophile N, are an alternative to hydride transfer energies for the classification of relative cation stabilities. The evaluation of $\Delta q(N)$ requires less computational effort, since an energy optimization of neutral reaction products in each single case is avoided. Further appealing prospects are the possibilities to discriminate between stabilities towards different nucleophiles which should allow to develop a more distinguished view on stabilities/reactivities in condensed phases, and to compare the electrophilicity of phosphenium ions with isoelectronic carbenes or silylenes.

(2) In addition to mesomeric E→P π-interactions, also the polarity of P−E σ-bonds exerts a relevant influence on the stabilities of phosphenium ions. In particular, the higher stabilizing effect of R_2N- as compared to RS-groups may be related to a balance of both contributions. The stabilities of heterocyclic cations with formal 6π-electron systems are further enhanced by cyclic conjugation. The energetic effect of this interaction is slightly higher than in the carbene or silylene system, but still significantly lower than the effect of N→P-π-interaction, or the electron delocalization energy in aromatic pholide anions. As in aminocarbenes,[21] cyclic π-conjugation in aminophosphenium ions therefore amplifies the energetic stabilization by N→P-π-interaction, but is not the primary stabilizing factor.

(3) Depending on the substituent pattern at phosphorus, phosphenium ions exhibit different frontier orbital sequences which resemble those of carbenes, heteroallyl anions, or phospholide anions. The failure to observe any changes in reaction patterns suggests that the reactivity is in all cases determined by the LUMO of the cation. In other words: phosphenium ions that are isolobal to heteroallyl or phospholide anions exhibit carbene analogue reactivity patterns because they always react as electrophiles rather than as nucleophiles (or ambiphiles), even in the complexation of transition metals. This implies that despite the isoelectronic and isolobal relationship between diaminophosphenium ions and *nucleophilic* diaminocarbenes, the observed reactivity patterns are better comparable to those of *electrophilic* carbenes

Experimental Section

All calculations were made with the Gaussian 94 package of programs.[27] Molecular geometries of cations **1−32**, the corresponding hydrogen substituted neutral compounds, carbenes and silylenes **33−36**, and the nucleophiles Me_3P and Me_3N were first energy optimized at the HF/6-31+g* level. Frequency analyses at this stage of optimization revealed that all structures except **17′** represent local minima on the energy hypersurface. Starting from these geometries, further energy optimizations were then carried

out at the MP2/6-31+g(d) level. The resulting final geometries were used for all subsequent calculations. The absolute electronegativity χ and absolute hardness η of **1−32**, Me_3P, and Me_3N were computed from orbital energies obtained with 6-31+g(d) basis sets. Because of the conceptual difficulties associated with the determination of electron affinities for anions,[5][28] the values of χ and η for the neutral atoms from ref.[5] were used for H^-, F^-, and I^-. Transferred charge densities $\Delta q(N)$ were then computed as described in the text. Values of ΔE_{GT} and ΔE_{deloc} were computed according to Eq. (1) and (3) at the MP2/6-31+g(d) and MP2/6-31+g(d)+ZPE level, respectively (zero point corrections were derived from additional frequency analyses at the MP2/6-31+g(d) level). The values of orbital populations and Wiberg indexes for **1−29**, and the atomic charges required for the calculation of ε were obtained from natural population analyses[16] of MP2 electron densities. Electrostatic factors ε were calculated as described. Representations of frontier orbitals were generated with the program MOLDEN.[29]

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