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Article

Structural Alternatives for the Formation of Halogenophosphine-Phosphenium Complexes

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NMR studies of reactions between some N-heterocyclic and acyclic diamino phosphenium ions $(R_2N)_2P^+$ and *P*-chlorophosphines $(R_2N)_2PCl$ suggest that the reactants interact via chloride scrambling rather than by formation of P–P bonded phosphenium-phosphine complexes. Computational studies of reactions between model ions $(R'_2N)_2P^+$ and neutral phosphines $(R'_2N)_2PX$ (X = F, Cl, Br) confirm that in the gas phase the formation of halide-bridged adducts is indeed preferred and only for the most electrophilic cation an alternative but energetically less favorable P–P bonded structure was found. The halide-bridged adducts feature nearly C_2-symmetrical P•••X•••P arrays (for X = Cl, Br) or are loose molecular complexes arising from electrostatic interaction between nearly unperturbed fragments (for X = F). In the latter case, a P•••F•••P-bridged structure was located as a transition state of a fluoride transfer reaction. The formation of the adducts appears to be controlled by electrostatic rather than orbital interactions. Consideration of solvent effects by a polarizable continuum model indicates a destabilization of the adducts versus the isolated fragments and suggests that in solution extensive dissociation occurs. The computations further reveal a large solvent-induced lengthening of the P–Cl bonds in N-heterocyclic halogenophosphines which implies that the unusual P–Cl distances observed for these species are, to a large part, attributable to intermolecular influences.

Introduction

Stable salts of phosphenium ions $[R_2P]^+$ [1,2] are accessible if the electron-deficient phosphorus atom is stabilized by donor substituents such as NR_2. The chemical reactivity of these ions is dominated by a pronounced ambiphilic nature which enables them to behave as both Lewis acid and Lewis base. The Lewis base character is manifested first in the formation of phosphenium complexes with transition metals that resemble in many aspects Fischer-type carbene complexes;[1−3] Lewis acid behavior has been established in cycloadditions to alkenes and alkynes[4−6] and the formation of isolable adducts with nucleophiles such as amines and phosphines.[7−18] The bonding in these adducts was described by a dualism between a phosphino-phosphonium species with a covalent P−P bond (**I**, Chart 1) and a phosphenium-

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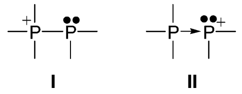
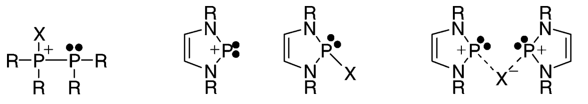
Chart 1



I II

Chart 2



III IV V VI

phosphine complex (**II**, Chart 1) with a coordinate bond that resembles the ligand−metal bond in a metal complex.[12] Experimental support for this view on phosphenium adducts as coordination compounds was provided by the finding that these species undergo ligand displacement reactions under exchange of one donor entity by another one.[12,14] Recent applications of this chemistry have opened synthetic access to cationic frameworks with polyphosphorus backbones[14,17,19] and enabled the use of phosphenium species as catalysts for P−C cross-coupling reactions.[20]

Although most isolated phosphenium-phosphine adducts contain tertiary phosphines as building blocks,[10,14,16,18] functional donors were employed as well. Particularly important in this respect is the formation of chlorophosphine-phosphenium adducts **III** (X = Cl, Chart 2) by the action of a strong Lewis acid on 2 equiv of a chlorophosphine.[18,21,22] This process can be formally described as two-step reaction involving first the interaction of 1 equiv of R_2PCl with the Lewis acid under P−Cl bond heterolysis to give a phosphenium ion which then forms a donor−acceptor complex with the second molecule of the phosphine. Since the practical synthesis of phosphenium salts is often carried out by the addition of a Lewis acid to a chlorophosphine precursor,[1] species of type **III** might be postulated as transient intermediates in these reactions.

During our studies of the chemistry of N-heterocyclic phosphenium ions,[23] we have recently reported that the cations **IV** (Chart 2) react with P−H substituted phosphines **V** (with X = H) under reversible transfer of a hydride.[24] Spectroscopic and computational studies suggested that this exchange proceeds via a transient hydride-bridged dimer **VI** (with X = H) that can be regarded as the structural isomer of a P−P bonded phosphenium-phosphine complex of type **III**. Considering that P···X···P-bridged adducts with topologies similar to that of **VI** may in principle be formed by the reaction of phosphenium ions with other functionalized phosphines, we have initiated a detailed study of the interaction of amino phosphenium species with the appropriate P-halogenated phosphines. The results, which are presented in this work, suggest that the formation of halide-bridged complexes of type **VI** can in fact be an alternative to the generation of the commonly observed P−P bonded phosphenium-phosphine adducts and allow some insight into the conditions under which one or the other type of structural isomer is formed.

Experimental Section

2-Chloro-1,3-bis-*tert*-butyl-1,3,2-diazaphospholene (**1a**[Cl], cf. **V** in Chart 2, R = ^{t}Bu, X = Cl) and 1,3-bis-*tert*-butyl-1,3,2-diazaphospholenium triflate (**1a**[OTf], cf. **IV** in Chart 2, R = ^{t}Bu) were synthesized as previously described.[24] Stock solutions were prepared by dissolving a weighed amount of each sample in a defined volume of dry dichloromethane. Appropriate volumes of these solutions were combined to produce mixtures of both components with defined molar ratios which were then characterized by ^{31}P NMR (Bruker Avance 400 spectrometer operating at 162.9 MHz, temperature 30 °C if not stated otherwise; chemical shifts vs ext. 85% H_3PO_4, $\Xi = 40.480747$ MHz). Attempts to characterize chlorophosphine adducts of further amino phosphenium ions were made by mixing $(i\mathrm{Pr}_2\mathrm{N})_2\mathrm{PCl}$ (**2a**[Cl]) and $[(\mathrm{CH}_2)_2\mathrm{N}(t\mathrm{Bu})]_2\mathrm{PCl}$ (**3a**[Cl]), respectively, with half a molar equivalent of silver triflate in dichloromethane. Attempts to isolate phosphenium-chlorophosphine adducts by crystallization at low temperature proved unfeasible.

DFT calculations were performed with the *Gaussian 03*[25] program suite using Becke's three-parameter exchange functional[26] with a Lee−Yang−Parr correlation energy functional (B3LYP); additional computations on key compounds were carried out using the hybrid functional of Perdew, Burke, and Ernzerhof[27] which employs 25% exchange and 75% correlation weighting (PBE1PBE) or the MPW1K functional.[28] In all cases, split-valence basis sets of double-ξ quality augmented by one set of polarization functions on all atoms and diffuse functions on all heavy atoms (6-31+g(d,p)) were used. Numerical integrations were performed on an ultrafine grid. Harmonic frequencies and zero-point energies calculated at the optimized gas-phase structures at the same level were used to verify that the structures were minima (only positive eigenvalues of the Hessian matrix) or transition states (one negative eigenvalue) on the potential energy surface and to compute Gibbs free energies at 298 K. Selected compounds were further studied at the MP2/6-31+g(d,p) level. Solvation effects were included at the SCRF level through the use of the COSMO model[29] as implemented in *Gaussian 03*. This formalism uses a polarizable continuum model in which a solvent cavity is created via a series of overlapping spheres. Dielectric constants of 8.39 and 36.64 corresponding to those of bulk dichloromethane and acetonitrile, respectively, were applied, and the gas-phase structures were reoptimized to obtain molecular structures and energetics in solution. The optimization runs for **3b**, **4b**[F], **4′b**[F], **4b**[Cl], **5b**[Cl], and **6b**[Cl] were done with less tight cutoff criteria; using the normal thresholds induced an oscillative behavior which was obviously related with problems in the construction of the solvent cavities and prevented the optimizations from converging. As the energies varied by less than 1 kcal mol^{-1} during the final optimization steps,

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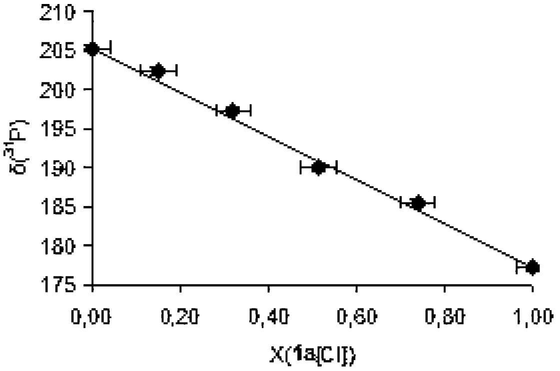

Figure 1. Plot of observed ^{31}P chemical shifts δ^{31}P vs molar fraction x(**1a**[Cl]) = c(**1a**[Cl])/(c(**1a**[OTf]) + c(**1a**[Cl])). Diamonds denote experimental data points with estimated standard deviations as error bars. The population weighted average calculated from the chemical shifts of the pure compounds is given as a straight line.

it is assumed that the maximum deviation of the reported energies from those at the true stationary points does not exceed this threshold. Analyses of electron populations were carried out with the natural bond order (NBO) module in *Gaussian 03*. Atomic coordinates and absolute energies are given as Supporting Information.

Results and Discussion

NMR Studies. The reaction of the N-heterocyclic chlorophosphine **1a**[Cl] and the phosphenium triflate **1a**[OTf] was studied by combining different volumes of stock solutions of each component at ambient temperature. ^{31}P NMR spectra of all mixtures displayed a single resonance whose position depended on the molar ratio **1a**[OTf]/**1a**[Cl] and was shifted continuously to lower field when the molar fraction of the phosphenium salt increased (Figure 1). Cooling to −70 °C resulted in some line broadening but did not give new signals. The observed behavior suggests that the reactants equilibrate via the intermolecular scrambling of a chloride ion at a rate at (or close to) the fast exchange limit, leading to coalescence of the individual lines into an average signal. The absence of signals attributable to AX-type spin systems and the finding that the observed line positions do not significantly deviate from the population weighted average of the shifts of the pure components (see Figure 1) allow the formation of the conclusion that noticeable amounts of P−P bonded phosphenium-phosphine adducts[10,18,22] are neither formed as stable products nor transient intermediates. Averaging of ^{31}P NMR signals was also observed for mixtures of the chlorophosphines **2a**[Cl] and **3a**[Cl] with the phosphenium triflates **2a**[OTf] and **3a**[OTf], which were prepared by reacting the former with one-half equivalent of silver triflate, indicating that these species also equilibrate via chloride scrambling. This behavior parallels previously reported reactions in which N-heterocyclic phosphenium ions were involved in intermolecular fluoride[23] or hydride[24] exchange, respectively.

Computational Studies. In order to obtain deeper insight into the halide exchange and to probe the possible involvement of P−P bonded adducts in this process, computational studies of the reactions of selected pairs of aminophosphenium ions and *P*-halogenophosphines were performed. As salts such as **1a**[OTf] exist in solution as solvent-separated ion pairs,[23] the focus was on describing the interaction of *P*-halogenophosphines with an isolated cation. To scale down the calculations, model compounds were employed in which the bulky N-alkyl groups of **1-3a**[Cl] had been replaced by methyl substituents. The computations were routinely performed at the B3LYP/6-31+g** level.

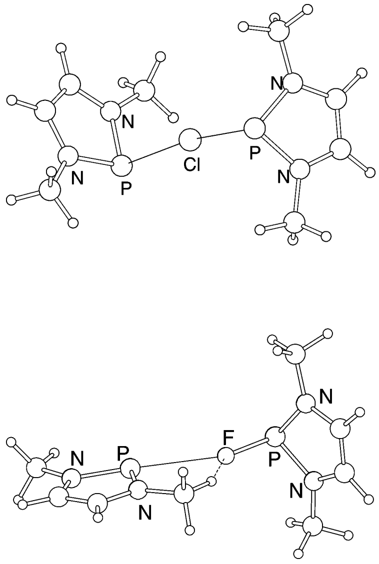

Figure 2. Ball-and-stick representations of the molecular structures of the phosphenium-halogenophosphine adducts **4b**[Cl] (top) and **4′b**[F] (bottom) computed at the B3LYP/6-31+g** level. The intermolecular P···X distances are drawn as thin solid lines, and a short intermolecular F···H distance in **4′b**[F] is drawn as a dashed line. Values of bond distances are listed in Table 2.

Attempts to determine an energy-optimized geometry for the gas-phase adduct of the cation **1b** with the chlorophosphine **1b**[Cl] inevitably produced the same molecular structure, which is best described as a C_2-symmetric chloro-bridged adduct **4b**[Cl] (Figure 2). The energy of this adduct, which marks the only located stationary point on the energy hypersurface, is 19.1 kcal mol^{-1} lower than the sum of energies of the fragments (see Table 1). The endocyclic bond lengths (Table 2) and the deviation of the rings from planarity range between the values seen in the data for cationic **1b** and neutral **1b**[Cl], whereas the P−Cl distances (2.768 Å) are clearly longer than those in **1b**[Cl] (2.341 Å). The coordination geometry of the chlorine atom is not linear as that in P···H···P-bridged phosphenium-phosphine adducts,[24] but distinctly bent (P−Cl−P 166.6°). NBO population analyses indicate a marked increase of negative charge on the chlorine atom (q(Cl) = −0.65) as compared with that of **1b**[Cl] (q(Cl) = −0.52) and imply that the ionic polarization of the P−Cl bond in the chlorophosphine[23] is further enhanced. The available data suggest that **4b**[Cl] is best described as a complex of a chloride anion which engages in the formation of two localized donor−acceptor bonds to two phosphenium ligands.

Similar results were obtained for the reaction of the cation **1b** with the bromophosphine **1b**[Br]. The only local minimum structure found corresponds in this case to a nearly C_2-symmetric Br-bridged complex **4b**[Br], which displays structural features similar to that of **4b**[Cl] (see Table 2; molecular structure not shown), but is formed in a reaction

Table 1. Number of Computed Imaginary Vibrational Frequencies (N_{Imag}) and Relative Energies (ΔE_{rel}(gas), $\Delta E_{\mathrm{rel}}(CH_2Cl)$), Solvation Energies ($\Delta E_{\mathrm{solv}}(CH_2Cl_2)$), and Free Enthalpies ($\Delta G^{298}_{\mathrm{rel}}$(gas), $\Delta G_{\mathrm{rel}}(CH_2Cl_2)$) with Respect to the Sum of Energies for the Isolated Cation and Halogenophosphine for the Cations **1b**−**3b**, the Halogenophosphines **1b**[X]−**3b**[X], and the Complexes **4b**[X]−**6b**[X] (X = F, Cl, Br) in the Gas Phase and in CH_2Cl_2 Solution. All Values Were Computed at the B3LYP/6-31+g(d,p) Level and Are Given in kcal mol^{-1}

	N_{Imag}	ΔE_{rel}(gas)	$\Delta G^{298}_{\mathrm{rel}}$(gas)	$\Delta E_{\mathrm{solv}}(CH_2Cl_2)$	$\Delta E_{\mathrm{rel}}(CH_2Cl_2)$	$\Delta G_{\mathrm{rel}}(CH_2Cl_2)$
1b	0			−46.9		
1b[F]	0			−6.6		
1b[Cl]	0			−12.9[a]		
1b[Br]	0			−11.3		
2b	0			−46.3		
2b[Cl]	0			−7.7		
3b	0			−45.0		
3b[Cl]	0			−6.5		
4′b[F]	0	−13.1	−4.4	−41.0	−0.7	1.4
4b[F]	1	−10.5	−1.1	−38.0	4.9	8.3
4b[Cl]	0	−19.1	−11.6	−42.2	−1.6	2.4
4b[Br]	0	−22.4	−14.8	[b]		
5b[Cl]	0	−19.0	−10.2	−37.7	−2.6	0.9
6b[Cl]	0	−16.4	−7.8	−36.2	−1.0	2.4
6′b[Cl]	0	−8.3	1.7	−40.4	2.8	8.3

[a] In CH_3CN, −15.9 kcal mol^{-1}. [b] No data available owing to convergence problems during the optimization run.

Table 2. Point Groups and Computed Endocyclic Bond Distances (in Å) for the Cations **1b**−**3b**, the Halogenophosphines **1b**[X]−**3b**[X], and the Complexes **4b**[X]−**6b**[X] (X = F, Cl, Br) in the Gas Phase and in CH_2Cl_2 Solution. All Values Were Computed at the B3LYP/6-31+g(d,p) Level

		gas phase		solution (CH_2Cl_2)			
	point group	$P{-}N_{(g)}$ $P'{-}N'_{(g)}$	$P{-}X_{(g)}$ $P'{-}X_{(g)}$	$P{-}N_{(solv)}$ $P'{-}N'_{(solv)}$	$P{-}X_{(solv)}$ $P'{-}X_{(solv)}$	Δ_{P-X}[a]	$\Delta_{P-X,rel}$ (%)[b]
1b	C_{2v}	1.695		1.693			
1b[F]	C_s	1.712	1.705	1.703	1.758	0.053	3.1
1b[Cl]	C_s	1.707	2.341	1.688[c]	2.863[c]	0.521	22.3
1b[Br]	C_s	1.709	2.501	1.689	2.928	0.427	17.1
2b	C_2	1.640		1.639			
2b[Cl]	C_1	1.682/1.699	2.276	1.680/1.660	2.468	0.192	8.5
3b	C_2	1.646		1.644			
3b[Cl]	C_1	1.700/1.700	2.246	1.679/1.679	2.413	0.166	7.4
4′b[F]	C_1	1.696/1.696	1.835	1.701/1.697	1.773	−0.062	−3.4
		1.703/1.708	2.768	1.701/1.696	3.122	0.355	12.8
4b[F]	C_2	1.688/1.687	2.142	1.687	2.146	0.004	0.2
4b[Cl]	C_1	1.691/1.691	2.768	1.698/1.699	3.031	0.263	9.5
		1.691/1.691	2.768	1.698/1.699	3.031	0.263	9.5
5b[Cl]	C_1	1.652/1.652	2.671	1.657/1.648	2.740	0.068	2.6
		1.660/1.660	2.675	1.656/1.646	2.789	0.114	4.3
6b[Cl]	C_1	1.660/1.660	2.688	1.657/1.658	2.70	0.012	0.5
		1.660/1.660	2.699	1.652/1.652	2.83	0.133	4.9
6′b[Cl]	C_1	1.671/1.718	2.228	1.668/1.710	2.342	0.114	5.1
		1.648/1.653	3.961	1.643/1.645	4.255	0.294	7.4

[a] $\Delta_{P-X} = P{-}X(CH_2Cl_2) - P{-}X(\mathrm{gas})$. [b] $\Delta_{P-X,rel} = \Delta_{P-X}/P{-}X(\mathrm{gas})$. [c] In CH_3CN: P−N = 1.688, P−Cl = 3.097, and Δ_{P-Cl} = 0.760 (32.3%).

that is slightly more exothermic ($\Delta E = -22.4$ kcal mol^{-1}). A different behavior was revealed, however, when the interaction of the fluorophosphine **1b**[F] with **1b** was considered. Attempts to determine an energy-optimized geometry in this case inevitably ended in a loose molecular complex **4′b**[F] (Figure 2). Even though a comparison of the intermolecular distances (P−F = 2.768 Å vs P−P = 4.439 Å) still justifies the classification of the adduct as a halogen-bridged complex, its structural properties clearly deviate from those of **4b**[Cl] and **4b**[Br] as the two P−F distances are now clearly unequal (1.834 and 2.768 Å), and the approach of the P−F bond does not occur perpendicular to the local coordination plane of the phosphenium unit but in this plane, to yield a nearly C_s-symmetric arrangement. The lengthening of the P−F bond in **4′b**[F] as compared with that of free **1b**[F] (Table 2) indicates a larger degree of $\sigma^*(P{-}F)/n(N)$ hyperconjugation but does not induce noticeable intermolecular charge transfer. Since the NBO results disclose the presence of sizable atomic charges on the phosphorus atom in the phosphenium fragment and the fluorine atom ($q(F) = -0.69$ and $q(P^+) = 1.43$ in **4′b**[F]), it appears that the assembly is charge controlled and the gain in energy of $\Delta E = -13.1$ kcal mol^{-1} associated with the formation of the adduct from **1b**[F] and **1b** presumably reflects the electrostatic (ion-dipole) interaction between both units.[30]

Further attempts to locate a F-bridged structure with a topology similar to that of **4b**[Cl] and **4b**[Br] finally led to a C_2-symmetric structure **4b**[F], which is higher in energy than **4′b**[F] ($\Delta E = -10.5$ kcal mol^{-1}) and represents a transition state rather than a local minimum. The negative eigenvalue of the Hessian matrix is associated with motion

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(30) This is further supported by the results of calculations of the electrostatic potential on the molecular surfaces of **1b** and **1b**[F] which indicates that the $P^+\cdots F$ interaction connects the regions of highest positive and negative electrostatic potential in both components (see Supporting Information).

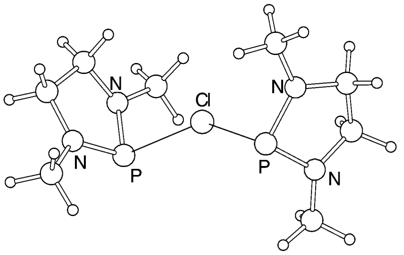

Figure 3. Ball-and-stick representation of the molecular structure of the Cl-bridged phosphenium-halogenophosphine adduct **5b**[Cl] computed at the B3LYP/6-31+g** level. The intermolecular P···X distances are drawn as thin lines. Values of bond lengths are given in Table 2.

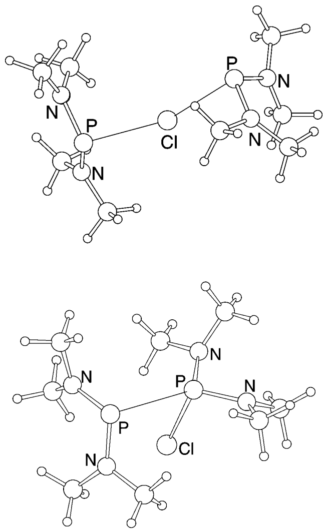

Figure 4. Ball-and-stick representation of the molecular structures of the adducts **6b**[Cl] (top) and **6′b**[Cl] (bottom) computed at the B3LYP/6-31+g** level. The intermolecular P···Cl and P···P distances are drawn as thin lines. Values of bond distances are given in Table 2.

of the fluorine atom along the P−P vector, which suggests that the calculated structure marks the transition state of a fluoride transfer between **1b** and **1b**[F].

Calculations similar to those for the pair **1b**/**1b**[Cl] were also carried out for the interaction of the cations **2b** and **3b** with the chlorophosphines **2b**[Cl] and **3b**[Cl], respectively. These efforts led to the identification of the nearly C_2-symmetric, chloro-bridged adducts **5b**[Cl] and **6b**[Cl] (see Figures 3 and 4; relevant bond distances are included in Table 2), which are both local minima on the energy hypersurface. The energetic stabilization of these adducts by 19.0 (**5b**[Cl]) and 16.4 (**6b**[Cl]) kcal mol^{-1} over the free fragments is similar to that in the case of **4b**[Cl]. Attempts to detect an alternative adduct with a P−P bonded structure failed for **5b**[Cl] (all searches always converged in the same local minimum) but in the case of **6b**[Cl] resulted in the location of a second isomer **6′b**[Cl]. The molecular structure (Figure 4) consists of two weakly bound fragments **3** and **3**[Cl] with an intramolecular P−Cl distance of 2.228 Å that is slightly shorter than that in free **3**[Cl] (2.246 Å) and an intermolecular P···Cl distance of 3.961 Å that clearly exceeds the P···P distance of 3.438 Å, thus justifying a formal description as a P−P bonded adduct. Although **6′b**[Cl] also represents a local minimum, it is some 8 kcal mol^{-1} higher in energy than the chloro-bridged isomer **6b**[Cl].[31] The standard computed Gibbs enthalpies of −8 to −15 kcal mol^{-1} $\Delta G^{298}_{rel}(g)$ for **4b**[Cl]−**6b**[Cl] and **4b**[Br] suggest that these complexes are stable entities in the gas phase and do not noticeably dissociate into the fragments, whereas the significantly lower value of $\Delta G^{298}_{rel}(g)$ for **4′b**[F] indicates that this species is only marginally stable.

Table 3. Energies of Formation of Halophosphine-Phosphenium Adducts for Different Computational Models. All Values Were Computed with 6-31+g(d,p) Basis Sets and Are Given in kcal mol^{-1}

	ΔE_{rel}(gas)			$\Delta E_{rel}(CH_2Cl_2)$		
	B3LYP	MPW1K	MP2	B3LYP	MPW1K	MP2
4′b[F]	−13.1	−14.0	−16.7	−0.7	−0.9	−7.0
4b[F]	−10.5	−12.7	−12.3	4.9	3.0	−0.1
4b[Cl]	−19.1	−20.1	−23.6	−1.6	−2.4	−2.5
6b[Cl]	−16.4	−17.2	−19.2	−36.2	−1.0	2.4
6′b[Cl]	−8.3	−11.2	−17.0			

In the light of some recent publications which demonstrated that the B3LYP model performed poorly in the prediction of the structures and energetics of Lewis acid−base complexes,[32,33] the molecular structures of the key compounds **4b**[F]/**4′b**[F], **4b**[Cl], and **6b**[Cl]/**6′b**[Cl] and the corresponding monomers **1b**, **1b**[F], and **1b**[Cl] were reoptimized at the MPW1K/6-31+g(dp) or MP2/6-31+g(dp) levels, respectively. The MPW1K functional[28] was designed to model transition states and has therefore been assumed to handle the "incomplete" bonding in donor−acceptor complexes more correctly.[32] Comparison of the final geometries (listings of atomic coordinates are given as Supporting Information) revealed that the molecular structures of the monomers **1b**, **1b**[F], and **1b**[Cl] and the adducts **4b**[F], **4′b**[F], and **6b**[Cl] showed only minor changes in bond lengths which reflect the differences between the computational models. The chloro-bridged adduct **4b**[Cl] displayed larger deviations of P−Cl distances which did not reveal a common trend, however. The P−P distance in the P−P bonded adduct **6′b**[Cl] is significantly shorter in both the MPW1K (P−P 2.960 Å) and MP2 (P−P 3.081 Å) levels than that in the B3LYP level (P−P 3.438 Å) whereas the "intramolecular" bond lengths change little.[34] The MPW1K and MP2 energies of formation of halide-bridged adducts are more negative than the B3LYP energies by 1−2 and 2−4 kcal mol^{-1}, respectively (cf. Table 3). In contrast, the energy of formation of the P−P bonded adduct **6′b** (−8.3 kcal mol^{-1} at the B3LYP level) is further lowered by some 3 kcal mol^{-1} at the MPW1K and by 9 kcal mol^{-1} at the MP2 level. These

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(31) Replacement of the methyl groups in **6′b** by H atoms results in shortening of the P−P distance to 2.370 Å and yields a more negative reaction energy ΔE_{rel} of −15.3 kcal mol^{-1} for $[(H_2N)_2P^+\cdots(Cl)(NH_2)_2]$, indicative of a strengthening of the dative P−P bond due to both a decrease in steric bulk and an increase in the electron-accepting power of the phosphenium fragment. Still, however, the P−P bonded adduct remains higher in energy than the corresponding P···Cl···P-bridged complex ($\Delta E = -19.2$ kcal mol^{-1} for $[(H_2N)_2P\cdots Cl\cdots P(NH_2)_2]^+$).

(32) Gilbert, T. M. *J. Phys. Chem. A* **2004**, *108*, 2550.

(33) LeTourneau, H. A.; Birsch, R. E.; Korbeck, G. J. L.; Radzkiewicz-Poutsma, *J. Phys. Chem. A* **2005**, *109*, 12014.

(34) A close inspection revealed that the MP2 and DFT structures further differ in displaying slightly different conformations. These deviations can be traced to changes in bond and torsional angles and are presumably attributable to the different handling of van der Waals or dispersion interactions in the different models.

trends suggest that the DFT models underestimate the energetic effect of the donor−acceptor P−P bond in **6′b** in relation to the phosphorus−halogen interaction in the other species. Even if this decreases the energetic separation between **6b** and **6′b**, the former remains the absolute minimum at all levels of theory studied, and the geometry optimizations gave no evidence for the existence of other stable isomers, as had already been found with the B3LYP model.

In view of the involvement of ionic species in the reactions under consideration, an analysis of gas-phase reactivities can hardly be expected to yield a realistic picture of the behavior of the reactants in solution where solvation must be considered to play an important, if not decisive, role. To take this aspect into account, the molecular structures and relative energies of all fragments and of the Cl-bridged adducts were recalculated with inclusion of solvation effects through the use of the COSMO formalism[29] as implemented in *Gaussian 03*.

Beside the minor changes to P−N distances, the structural effects of solvation are reflected in a substantial elongation of P−X bonds (see Table 2). Quite surprisingly, this lengthening affects not only intermolecular distances in the adducts **4b**[Cl]−**6b**[Cl] but even more so the intramolecular P−X bonds in the halogenophosphines **1b**[Cl]−**3b**[Cl]. Thus, the largest effect is found in **1b**[Cl] ($\Delta_{P-Cl} = 22.3\%$ relative to the distance in the gas phase), and the perturbation decreases in **2b**[Cl] ($\Delta_{P-Cl} = 8.5\%$) and **3b**[Cl] ($\Delta_{P-Cl} = 7.4\%$). Analogous structural effects were also noted for **1b**[X] (X = Br, F) even though the degree of solvent-induced lengthening of P−Br and P−F bonds is less pronounced than that in **1b**[Cl] (Table 2). A further increase of the bond lengthening in **1b**[Cl] is found when the dielectric constant of the solvent is raised from $\epsilon = 8.93$ (bulk CH_2Cl_2) to $\epsilon = 36.64$ (CH_3CN; $\Delta_{P-Cl} = 32.3\%$). Preliminary studies indicate that the individual P−X bond lengths as well as their solvent-induced variation strongly depend on the chosen computational model; e.g., the relative lengthening of the P−Cl distance in **1b**[Cl] is smaller when the PBE1PBE ($\Delta_{P-Cl} = 14.6\%$) and MPW1K functionals ($\Delta_{P-Cl} = 13.3\%$) are used instead of B3LYP and still larger when the MP2 model is employed ($\Delta_{P-Cl} = 41.8\%$, P−Cl = 3.250 Å).

Comparison of the computed energy differences between molecules in the gas phase and in CH_2Cl_2 solution (ΔE_{solv} in Table 1) reveals that the cations **1b**−**3b** exhibit far larger stabilization by solvation effects (ΔE_{solv} 45−50 kcal mol^{-1}) than the neutral phosphines **1b**[X]−**3b**[X] ($\Delta E_{solv} < 10$ kcal mol^{-1}) which presumably reflects the difference in charges. The magnitude of ΔE_{solv} for **4b**[X]−**6b**[X] (38−42 kcal mol^{-1}) is slightly but systematically lower than that for **1b**−**3b**, which is rationalized by considering that the adducts have the same overall charge but exhibit larger molecular volumes and thus lower average charge densities. Regarding all effects simultaneously reduces the relative stability of the reactants **1b**[X]−**3b**[X]/**1b**−**3b** to an extent that the energies for the formation of the adducts **4′b**[F] and **4b**[Cl]−**6b**[Cl] (ΔE_{rel}(soln) in Table 1) remain just negative, and the formation of **4b**[F] and the P⋯P bonded complex **6b**[Cl] becomes endothermic. Calculation of the difference in free energy in solution between starting materials and adducts (ΔG_{rel}(soln) in Table 1) gives positive numbers in all cases but conserves the energy relations between the pairs of structural isomers **4b**[Cl]/**4′b**[Cl] and **6b**[Cl]/**6′b**[Cl]. Computation of the appropriate energies of key compounds using the MPW1K or MP2 models (Table 3) reveals that regardless of numerical deviations the same trends are reproduced at all levels of theory. If one considers that the values of ΔG_{rel}(soln) should allow a better estimate for the equilibrium constant of the complex formation reaction than those of ΔE_{rel}(soln), these results suggest that all complexes dissociate extensively in solution and should presumably not be regarded as stable compounds but as transient intermediates or at best minor components in a dynamic equilibrium.

On the whole, the computational results suggest that reactions of diaminophosphenium ions with halogenophosphines give halide-bridged adducts instead of P−P bonded phosphino-phosphenium species, as commonly observed in similar reactions.[18,21,22] Depending on the nature of the halide X, the products may be formulated as weakly bonded bimolecular aggregates that are held together by electrostatic interactions (X = F) or as halide-bridged dimers (X = Cl, Br). The latter are structurally closely related to hydride-bridged adducts[23] but differ in the respect that the bonding in the P⋯X⋯P unit is maintained by two localized (dative) bonds rather than a delocalized two-electron-three-center bonding interaction. Evidence for the existence of a P−P bonded phosphino-phosphenium complex involving a direct covalent phosphorus−phosphorus interaction was only obtained in the case of the acyclic cation **3b**, and this structure was predicted to be higher in energy than a halide-bridged isomer. The computed energies further suggest that the halide-bridged complexes can be regarded as stable species in the gas phase whereas their stability in solution is adversely influenced by solvation effects, and extensive dissociation is foreseen. These predictions are in excellent agreement with the actually observed behavior of mixtures of phosphenium salts and chlorophosphines and provide a mechanistic interpretation for the found chloride exchange reactions up to the point that the absence of detectable reaction intermediates may be accounted for. The facts that **3b** is the strongest electrophile in the series of cations studied[35] and that the P−P bonding interaction in the adduct **6′b**[Cl] appears to increase upon formal replacement of the methyl substituents by hydrogens[31] suggest that the adduct structure decisively depends on the Lewis acidity of the phosphenium ion. This line of reasoning had already been followed to explain the preference of hydride-bridged over P−P bonded diazaphospholenium-diazaphospholene complexes[24] and is also in accord with the known situation that the most stable P−P bonded phosphenium-halogenophosphine adducts involve acceptor cations of high Lewis acidity[36] whereas adducts of diaminophosphenium cations are intrinsically much more labile and require strongly nucleophilic phosphines[10] (e.g., PMe_3) or the presence of

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(35) Gudat, D. *Eur. J. Inorg. Chem.* **1998**, 1087.

additional forces (e.g., π-stacking interactions)[18] in order to prevent dissociation.

A remarkable aspect of the reaction between the cations **1b**−**3b** and the donors **1b**[X]−**3b**[X] is that the preference for the formation of halide-bridged complexes disagrees with predictions derived from a frontier orbital analysis: As both the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor fragment can be regarded as essentially representing a lone pair at one phosphorous atom and an empty p orbital at the second phosphorus atom, the orbital-controlled interaction of both fragments is expected to yield a P−P bonded adduct. The formation of the actually observed halide-bridged complexes is best rationalized by assuming that the approach of the reactants is directed, rather, by electrostatic interactions, and the reaction thus proceeds under charge control. Charge-controlled reactivity can be considered a typical feature of "hard" Lewis acids and bases,[37] and such behavior is in good accord with the trend that increasing stability of a phosphenium ion correlates with an increase in the HOMO−LUMO gap,[35] which renders the cation less polarizable and thus "harder".

A dominance of electrostatic aspects is further highlighted if one considers the structural effects of solvation in the compounds under study. The solvent-induced lengthening of both intermolecular P···X distances in the adducts **4b**[F] and **4b**[Cl]−**6b**[Cl] and intramolecular P−X bonds in the halogenophosphines **1b**[X]−**3b**[X] is interpreted in simple terms as a consequence of the attenuation of attractive electrostatic forces in a dielectric medium and is seen as straightforward confirmation of a substantial ionic bonding contribution. Although quantitative assessment of the degree of solvent-induced bond lengthening is yet prevented by the strong dependence on the chosen computational model, the results allow one to state that the effect is exceptionally large in the case of **1b**[Cl]. This finding confirms the previous attribution[23] of a particularly high degree of P−Cl bond ionicity in N-heterocyclic chlorophosphines of this type and is further evidence of importance, as it suggests an explanation for the known discrepancy[23] between experimentally determined (solid state) and computed (gas phase) molecular structures for these species: If one considers the set of neighbors of an individual molecule in a crystal as a polar (owing to the presence of sizable dipole moments) "solvent", the "solute" experiences a polarizing effect similar to that in a real solution, and the unique bond lengthening observed in the crystal structures of **1a**[Cl] and related derivatives is to a great extent attributable to P−Cl bond polarization by intermolecular rather than intramolecular influences. The practical importance of these effects is highlighted by the peculiar deviations in P−Cl bond lengths in the crystal structures of **1a** and its toluene solvate[23] and the large solvent dependence of the ^{31}P NMR chemical shift of these compounds.[23,38] Furthermore, these results further support the view[23] that the P−Cl bonds in *P*-chlorodiazaphospholenes display, in the sense of the formal definition by A. Haaland,[39] distinctive characteristics of a dative bond between a phosphenium cation and a chloride anion.

Conclusions

Experimental and computational evidence supports the tenet that diaminophosphenium ions and diaminochlorophosphines do not react to give P−P bonded complexes, which have been obtained as stable compounds in reactions of phosphenium species of higher Lewis acidity. The computational studies instead suggest that transient P···X···P halide-bridged complexes are formed, which are observed in the case of X = Cl, Br, and structurally related to the corresponding hydride-bridged derivatives. The occurrence of these intermediates permits consideration of the observed ligand exchange between phosphenium ions and phosphines as electrophilic substitution at a halide center and provides an alternative mechanistic explanation of this process that complements previously established S_{N1}- and S_{N2}-type reactions at the low-coordinate phosphorus atom.[18]

The interaction between the fragments in the P···X···P-bridged complexes appears to be controlled by electrostatic interactions. The influence of dipolar solvents markedly reduces the stability of the adducts and facilitates dissociation. Furthermore, solvation exerts a structural effect in inducing a lengthening of phosphorus−halogen bonds, which is most prominent for the N-heterocyclic derivative **1b**[Cl] with high bond ionicity. These results allow one to attribute features such as the extraordinarily large P−Cl distances in crystalline specimens or the unique solvent dependence of NMR chemical shifts to intermolecular influences. The finding of similar—albeit smaller—effects of intermolecular polarization for the chlorophosphines **2b**[Cl] and **3b**[Cl] suggest that the phenomenon may also affect other compounds with polar element−halogen bonds. Even if the dependence of the solvent-induced structural and energetic changes on the chosen computational model prevents as yet a precise forecast of the magnitude of these effects, the presented results emphasize that it is important to include solvation effects if precise predictions of molecular structures and energetics of these species are desired.

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Supporting Information Available: Complete ref 25; computational details (extended geometric and energy data). This material is available free of charge via the Internet at http://pubs.acs.org.

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(36) A vivid example is the formation of the complex [$Me_2N(Cl)$-P···$P(NMe_2)_3]^+$ during the reaction of $(Me_2N)_2PCl$ with $AlCl_3$, as this product represents the combination of the most Lewis acidic phosphenium ion with the most basic phosphine; cf. ref 21.

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