DOI: 10.1002/chem.200902931

Towards Spontaneous Heterolysis of the Homonuclear P−P Bond in Diphosphines: The Case of Diazaphospholeniumtriphospholides

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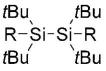
Abstract: Computational studies on a series of polyphospholyl-substituted N-heterocyclic phosphines $(CH)_2(NR)_2P{-}P_n(CH)_{5-n}$ (R = Me, n = 1–5) disclosed that increasing formal replacement of CH units in the phosphole ring by phosphorus atoms is associated with an increase in P−P distances and charge separation, and a decrease in covalent bond orders. Altogether, these trends imply that the CH versus P substitution enhances ionic P−P bond polarization in these compounds. Experimental verification of this hypothesis was obtained for the triphospholyl diazaphospholenes $(CR)_2(NR')_2P{-}P_3(C\mathit{t}Bu)_2$ (**8a**: R = H, R′ = *t*Bu; **8b**: R = Me, R′ = Mesityl [Mes]), which were prepared through metathesis reactions from suitable precursors and identified by solution and solid-state NMR data and a single-crystal X-ray diffraction study of **8a**. Analysis of J_{PP} coupling patterns suggested that both species are characterized by the absence of a strong covalent P−P bond connecting both rings. This interpretation was confirmed by the finding of a unique P−P distance of 2.79 Å for crystalline **8a**, and further supported by computational studies, which led to the conclusion that both species are better described as diazaphospholenium-triphospholide contact ion pairs rather than covalent molecules. Variable-temperature (VT) NMR spectra of **8b** showed a collapse of J_{PP} couplings between atoms in different rings, which indicates scrambling of the diazaphospholenium and triphospholide units between different molecules in solution, and further substantiates the proposed view on the molecular structure.

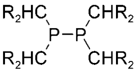
Keywords: bond polarization • density functional calculations • diphosphines • NMR spectroscopy • phosphorus • X-ray diffraction

Introduction

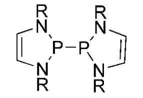
The interest in studies of sterically distorted or electronically highly polarized molecules is often motivated by the realization that unusual structures may trigger unprecedented physical or chemical properties that are hardly known for undistorted molecules.[1] An interesting example of structural distortions and their chemical consequences is provided by compounds like the disilanes **1a** (R = H, Si−Si 2.43 Å,[2]) and **1b** (R = *t*Bu, Si−Si 2.697 Å[3]) or the diphosphine **2** (P−P 2.310 Å[4]), in which a central single bond connects two atoms that carry extremely bulky substituents. The steric congestion in these molecules induces not only an elongation of this E−E bond to values far beyond a standard single bond length (Si−Si 2.359(12) Å, P−P 2.214(22) Å[5]) but also an interesting reactivity: whereas disilanes and diphosphines are usually thermally quite stable, **1** and **2** react easily with homolytic bond cleavage to give persistent radicals.[4,6] It has



1a (R = H)
1b (R = *t*Bu)



2 (R = SiMe$_3$)



3 (R = *t*Bu, Mes)

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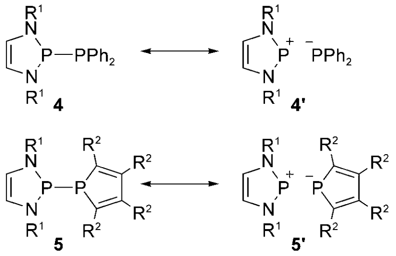
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200902931.

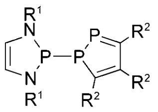
been demonstrated recently for the heterocyclic diphosphines **3** that bond cleavage is further facilitated if the formed radicals are stabilized by π delocalization.[7]

We reported some time ago on unsymmetrically substituted diphosphines **4** and **5**[8–10] (Scheme 1) with P–P bonds that are similar to or even longer (2.35–2.70 Å) than those in **2** and **3**. These compounds also display quite unusual chemical properties, and react under very mild conditions through the addition of the P–P bond to alkynes and alkenes (diphosphination),[8,11] or through metal-assisted activation of nitriles.[9] The unique structural features and reactivities were ascribed to ionic polarization of the intrinsically nonpolar P–P bond by means of a push–pull substitution scheme, which can be depicted by bond/no-bond resonance between covalent (**4**/**5**) and ionic (**4′**/**5′**) canonical structures (Scheme 1).[8–10] A particularly marked P–P bond lengthening for **5** was assumed to reflect the enhanced weight of the ionic canonical structure, which arises as a result of aromatic stabilization in both the phospholyl anion[12] and the N-heterocyclic phosphenium cation fragment,[13] and led to the portrayal of these species as hybrids between covalent molecules and phosphenium–phospholide contact ion pairs. Consequently, the P–P bond is best described as a dative donor–acceptor bond[14] rather than a "normal" covalent interaction. However, even if the bond polarization introduces a sizeable charge separation and strengthens the electrostatic contribution to the bond energy, the covalent interaction remains still dominant.[10]



Scheme 1. Unsymmetrically substituted diphosphines; $R^1 = t$Bu, Mes, 2,6-$Me_2C_6H_4$; $R^2 = Et$.

In the light of these findings, it remains a great challenge to overturn the described situation by preparing diphosphines that exhibit P–P bonds of a predominantly ionic nature, and might thus represent a still closer approach to true "phospheniumphosphides". Since the stabilization in polyphospholide ions increases with the number of phosphorus atoms,[15,16] it is expected that replacing one or more CH units in the phosphole ring by phosphorus atoms would result in relative enhancement of the **5′** type structures, and might thus permit the fine tuning of P–P bond ionicity in **5**/**5′**. We identified, therefore, diazaphospholeniumpolyphospholides **6**–**11** as interesting target compounds in the quest for ionic phospheniumphosphides. Here, we report on computational studies on **5H**–**11H** (with $R^{1,2} = H$) and the P–C_5H_5-substituted derivative **12H**, which support the validity of our approach, and on the reactions of *P*-chlorodiazaphospholenes with a sodium triphospholide, which gave evidence that the expected products are in fact accessible and exhibit interesting structural and spectroscopic properties.



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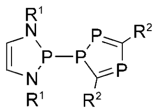

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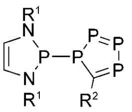

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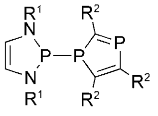

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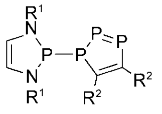

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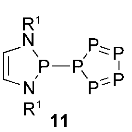

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Results and Discussion

Computational studies of the bond polarization in diazaphospholeniumpolyphospholides: A theoretical assessment of the effect of CH/P-substitution in the phospholyl ring on P–P bond polarization was derived from a comparison of computed molecular structures and electron distributions of diazaphospholeniumpolyphospholides **5H**–**11H** and the cyclopentadienyl derivative $(CH)_2(NH)_2P{-}C_5H_5$ (**12H**), and an analysis of the energetics of dissociation and isodesmic ligand exchange reactions. Optimization runs allowed the identification, for all compounds, of several conformers or structural isomers separated by rather small energy differences (0.5–8.9 kcal mol^{-1}). The most stable structures, all of which represent local minima, are displayed in Figure 1, and

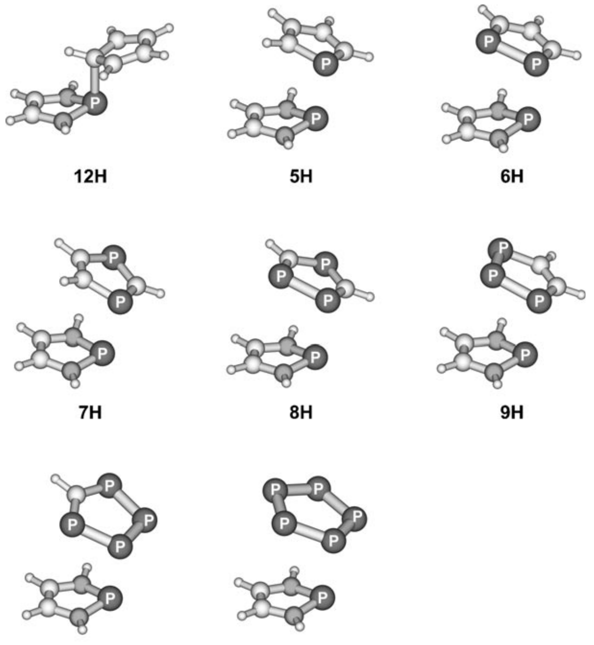


Figure 1. Molecular structures of the most stable conformational isomers of **5H**–**12H** computed at the B3LYP/6-311+G** level of theory.

a complete listing of all isomers and their relative energies at the B3LYP/6-311+G** and MP2/6-311+G**//B3LYP/6-311+G** levels of theory is given in the Supporting Information.

The energy difference between isomers was calculated using MP2/6-311+G** single-point calculations, and for the smaller systems (**12H** and **5H**) MP2/aug-cc-pVDZ and highly accurate CBS-QB3 calculations (on B3LYP/6-311+G** geometries) were performed. The B3LYP/6-311+G** relative energies are in perfect agreement with the CBS-QB3 results. However, the MP2 level overestimates the stability of P–C bonded isomers (they are usually found to be only 2–4 kcal mol^{-1} less stable than P–P bonded isomers at the MP2/6-311+G**//B3LYP/6-311+G** level, see later).

Polyphospholyl-substituted N-heterocyclic phosphines can, in principle, be assigned to one of two basic types, depending on whether the rings are linked by P–P or P–C bonds, respectively. Our calculations indicate that for all compounds **5H**–**11H**, a P–P bonded isomer is the most stable structure; P–C bonded species were predicted to have distinctly higher energies (Gibbs free energy differences of 7–8.3 kcal mol^{-1}) and were in several cases not even local minima on the energy hypersurface, indicating a clear preference for connection of the rings through P–P bonds. Whereas in previous experimental and computational studies on more heavily-substituted *P*-cyclopentadienyl-[17] and *P*-phospholyldiazaphospholenes (**5**, $R^{1,2} \neq H$)[10] *trans*-rotamers had always been identified as conformational ground states, for **5H**–**11H** several energetically very similar conformers (see Supporting Information) were located, suggesting that the steric demand of substituents may dictate the conformational preference.

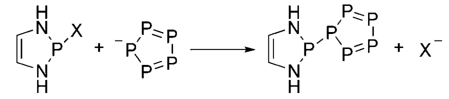
Since the energy differences between P–P and P–C bonded isomers in **6H**–**11H** are less than 10 kcal mol^{-1}, and the barrier for the diazaphospholene shift is significantly smaller (5–6 kcal mol^{-1} for **11H** and **12H** at B3LYP/6-311+G**, see Supporting Information) than for the shift of a PH_2 group on cyclopentadiene (20.8 kcal mol^{-1}, compare reference [18]), both findings may be taken as hints towards a substantial ionic bonding contribution. This idea is further supported by comparison of calculated bond lengths and Wiberg bond indexes (WBI) for the central P–P bonds in the most stable conformers of **5H**–**11H** (Table 1), which discloses a general bond lengthening and concomitant decrease in covalent bond order with an increasing number of phosphorus atoms in the polyphosphole ring (**10H** being the only exception from a strictly monotonous sequence). The computed electron densities, ρ, and their Laplacians, $\nabla^2(\rho)$, at the bond critical point, as obtained from Bader analysis of the B3LYP/6-311+G** electron density (Table 1), display generally small positive values, which are typical for a predominantly ionic bonding situation, and decrease further with increasing bond distance, thus emphasizing that the growing spatial separation of the two five-membered rings does indeed correlate with increasing bond polarization.

Table 1. Listing of P–P bond lengths (P–P), Wiberg bond indexes (WBI), electron density (ρ), and its Laplacian ($\nabla^2(\rho)$) at the bond critical point, and energies ΔE_{diss} and Gibbs free energies ΔG_{diss} for **5H**–**11H** computed at the B3LYP/6-311+G** level of theory.

	P–P [Å]	WBI	ρ [a.u.]	$\nabla^2(\rho)$ [a.u.]	ΔE_{diss} [kcal mol^{-1}]	ΔG_{diss} [kcal mol^{-1}]
5H	2.508	0.600	0.116	−0.140	113.5	102.1
6H	2.544	0.568	0.068	−0.005	103.1	92.0
7H	2.586	0.506	0.062	0.006	103.3	92.5
8H	2.611	0.493	0.058	0.011	95.6	85.0
9H	2.601	0.499	0.055	0.017	95.8	85.0
10H	2.593	0.527	0.055	0.016	88.9	78.7
11H	2.675	0.447	0.057	−0.004	83.3	74.2

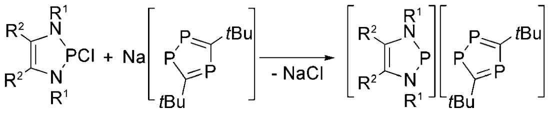
To investigate the energetics of the P–P bond cleavage, we also calculated the energies (ΔE_{diss}) and Gibbs free energies (ΔG_{diss}) for the dissociation of the most stable conformers of **5H**–**11H** into separate cyclic phosphenium and (poly)phospholide ions at two levels of theory (Table 1). To eliminate the difficulties associated with the charge separation of oppositely charged ions in the gas phase, reaction energies ΔE_{GT} for the isodesmic group transfer reaction were also computed (Table 2). The observed parallel trends in all three energy measures reflect that the energy required for the charge separation declines continuously with increasing number of phosphorus atoms in the polyphosphole ring (the only exception being again **10H**), whereas the positions of the phosphorus atoms in the ring seems to be of little importance. In connection with the observed bond lengthening, these trends suggest that the P–P bond is substantially weakened, and the dissociation into ionic fragments is facilitated with an increasing degree of phosphorus substitution in the polyphosphole ring.

Table 2. Computed (at the B3LYP/6-311+G** level) reaction energies ΔEGT for the shown isodesmic group transfer reaction.



X	ΔE_{GT} [kcal mol^{-1}]	X	ΔE_{GT} [kcal mol^{-1}]
C_5H_5	38.1	1,2,4-$P_3(CH)_2$	12.5
$P(CH)_4$	30.2	1,2,3-$P_3(CH)_2$	12.3
1,2-$P_2(CH)_3$	20.1	1,2,3,4-$P_4(CH)$	5.7
1,3-$P_2(CH)_3$	19.8	P_5	0.0

Reactions of *P*-chlorodiazaphospholenes with a sodium triphospholide: Reactions between appropriate amounts of *P*-chloro N-heterocyclic phosphines **13a**,**b**[19] and the triphospholide $[P_3C_2tBu_2][Na(thf)_x]$[20,21] at room temperature in anhydrous THF produced the metathesis products **8a**,**b** (Scheme 2). Both compounds were isolated after work-up as deep yellow, highly air- and moisture-sensitive solids, readily soluble in anhydrous aromatic hydrocarbons, THF, or acetonitrile, but poorly soluble in aliphatic hydrocarbons, and characterized by elemental analysis, NMR and, in the case of **8a**, a single-crystal X-ray diffraction study.



8a,b

Scheme 2. **8a**: $R^1 = t\mathrm{Bu}$, $R^2 = \mathrm{H}$; **8b**: $R^1 = \mathrm{Me}$, $R^2 = \mathrm{Mes}$.

Crucial information for the assignment of the constitution and dynamics of **8a**,**b** was derived from solution and solid-state ^{31}P NMR spectra. The ^{31}P cross-polarization magic-angle-spinning (CP-MAS) spectrum of solid **8a** displays four spinning sideband manifolds. The lines of two sideband systems exhibit doublet structures due to mutual coupling, and are readily assigned to the directly connected phosphorus atoms in the triphosphole ring ($^1J_{PP} = 450$ Hz). A *J*-resolved 2D-NMR spectrum (see Supporting Information) discloses for the lines of a third sideband system a triplet structure that is not resolved in the 1D-NMR spectrum. The size of this coupling (55 Hz) compares well to values of $^2J_{PP}$ in known triphosphol(id)es,[20–23] and the signal is readily assigned to the isolated phosphorus atom in the triphosphole ring. The lines in the last sideband pattern appear even in the *J*-resolved spectrum as singlet, and the clear assignment to the phosphorus atom in the diazaphospholene ring is supported by the similarity of the chemical shift ($\delta = 167$ ppm) with those of known phospholyl-1,3,2-diazaphospholenes **5** ($\delta = 135$–170 ppm).[8,10,11]

The solution ^{31}P NMR spectrum of **8a** is temperature-dependent and consists, above 70 °C, of two multiplet that belong to an AX_2 spin system ($\delta_A = 274.4$, $\delta_X = 225.9$ ppm, $J_{AX} = 45$ Hz) and are assigned to the phosphorus atoms in the P_3C_2 ring, and a singlet around $\delta = 157$ ppm for the phosphorus atom in the N-heterocycle. The two lines at lowest field broaden when the temperature is lowered, and the X_2 signal decoalesces eventually into two signals of equal intensity so that the spectrum displays at −100 °C four resonances with similar chemical shifts ($\delta = 278$, 231, 202, 155 ppm, Figure 2) to those observed in the solid state ($\delta = 260$, 238, 226, 167 ppm).

The temperature-dependent changes suggest that **8a** behaves in solution as a fluxional molecule, which exists in the slow-exchange limit (and in the solid state) as 1-substituted triphosphole, and undergoes degenerate suprafacial [1,5]-sigma tropic shifts of the diazaphospholenyl moiety at higher temperature. Although similar molecular structures and dynamics had previously been observed for R_3Sn-substituted triphospholes **14** (Scheme 3),[20,24] there are some striking differences between both types of molecules. Thus, the tricoordinate phosphorus atom in the P_3C_2 ring of **14** displays, in the slow-exchange limit, a much lower chemical shift than the dicoordinate phosphorus atoms (e.g., $\delta(\mathrm{P1}) = 30$ vs. $\delta(\mathrm{P2,4}) = 270$–$320$ ppm in **14a**) and a large $^1J_{PSn}$ coupling constant.[20] In contrast, the chemical shifts of all three phosphorus atoms in the P_3C_2 ring of **8a** remain similar ($\delta = 202$–278 ppm), and the failure to resolve a $^1J_{PP}$ coupling across the P−P bond between both rings indicates that the size of this coupling is distinctly smaller than the common values of 100–400 Hz in acyclic diphosphines.[25] ^{31}P Chemical shifts between $\delta = 200$ and 300 ppm for triphosphole derivatives are characteristic for ionic species like the alkaline and alkaline-earth metal salts (e.g., $\mathrm{K[P_3(C}t\mathrm{Bu)_2]}$: AB_2 spin system with $\delta_A = 252.8$, $\delta_B = 242.8$ ppm), in which the π-electron delocalization is preserved and all phosphorus atoms remain two-coordinate.[21–23] Furthermore, we had shown that a decrease of $^1J_{PP}$ in *P*-phospholyl-1,3,2-diazaphospholenes coincides with a lengthening of the P−P bond, and had predicted that $^1J_{PP}$ should vanish if the P−P distance came close to a value of 2.8 Å.[10] Considering all arguments together, we conclude that solid **8a** exhibits a similar P−P bonded topology as **5** in connection with an even more pronounced ionic P−P bond polarization.

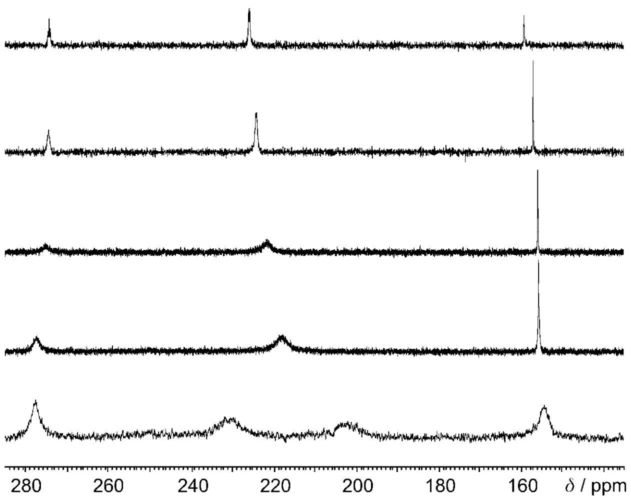
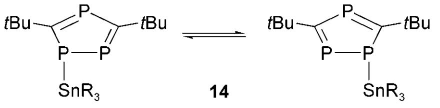


Figure 2. ^{31}P{^{1}H} NMR spectra of a [D$_8$]toluene solution of **8a** recorded at (from top to bottom) 343, 303, 253, 213, 173 K.



Scheme 3. R_3Sn-substituted triphospholes with fluxional structures; R = Ph (**14a**), Me (**14b**), Bu (**14c**).

This hypothesis was fully confirmed by the results of a single-crystal X-ray diffraction study. The crystal contains isolated molecular units (Figure 3), which contain nearly planar triphosphole and diazaphospholene rings (largest deviations from the least square planes through all ring atoms are 0.05 Å for the P_3C_2 and 0.07 Å for the PN_2C_2 rings). The shortest contact between both rings (P1−P15 2.793(1) Å) is longer by some 0.09 Å than the longest known P−P bond in *P*-phospholyl-1,3,2-diazaphospholenes **5** (2.701(2) Å),[10] nearly 0.60 Å longer than a standard P−P single bond (2.21 Å),[5] and exceeds even distances in compounds with "one-electron bonds" (2.43–2.63 Å) in which two phosphorus atoms are formally connected by a single bonding electron.[26] The molecular structure of **8a** differs from those of the *P*-phospholyl-diazaphospholenes **5**[8,10] by showing a

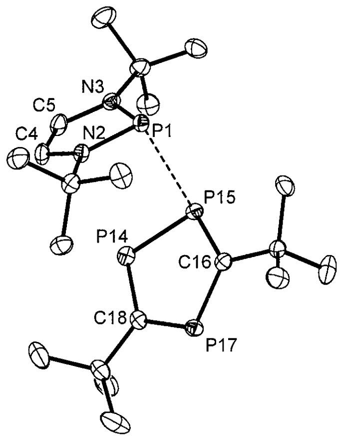


Figure 3. Molecular structure of **8a** (H atoms and solvent molecules omitted for clarity; 50 % probability thermal ellipsoids); selected bond lengths [Å]: P1–N3 1.675(2), N3–C5 1.385(3), C5–C4 1.341(3), C4–N2 1.380(3), N2–P1 1.671(2), P1–P15 2.793(1), P15–P14 2.112(1), P14–C18 1.741(2), C18–P17 1.750(2) , P17–C16 1.735(2), C16–P15 1.748(2).

gauche rather than *trans* alignment of the two rings, and by a substantial widening of the bond angles around P15 (P14-P15-P1 101.1°, C16-P15-P1 115.7° vs. P-P-C $<90°$ in **5**); both features are presumably enforced by the steric interference between the bulky *tert*-butyl substituents on both rings.

The bonds in the diazaphospholene ring of **8a** (see Figure 3) resemble more closely the distances in diazaphospholenium cations (P–N 1.66–1.69, N–C 1.36–1.39, C–C 1.34–1.38 Å[19]) with a delocalized 6π-electron system than those in neutral diazaphospholenes, in which bond order alternation is more pronounced.[19] The P14–P15 distance (2.112 Å) is halfway between a single and double bond, and all phosphorus–carbon bonds in the P_3C_2 ring fall into the narrow range between 1.735 and 1.750 Å. Similar distances are found in triphospholide salts such as $Sr[\{P_3(CtBu)_2\}_2]$ (P–C 1.745–1.759 Å[22]) and $Cs[P_3(CMes^*)_2]$ (P–C 1.727–1.744 Å[23]), or η^5-bound complexes such as $M[P_3(CMes^*)_2]$ (M = In, Ga, P–C 1.75–1.78 Å; M = Tl, P–C 1.75–1.77 Å[22]), which possess strongly delocalized π-electron systems. In contrast, the (η^1-triphospholyl)stannane **14a**[20] contains an array of alternating short (1.698(5), 1.712(5) Å) and long (1.773(5), 1.785(5) Å) P–C bonds, which is in accord with its diene-like reactivity, and suggests that the covalent interaction of one atom in the triphospholyl unit with a stannyl substituent triggers perceptible π-electron localization.[27]

The structural features of **8a**, with a combination of pronounced bond length equalization in the rings and an extraordinarily long connecting bond, support the view that **8a** should be regarded, like **5**,[10] as a contact ion pair of a triphospholide anion and a diazaphospholenium cation. This view is also backed by the results of a computational study on **8a**. Geometry optimization at the B3LYP/6-31+G* level of theory produced two molecular structures (graphical representations and listings of atomic coordinates are given as Supporting Information). One structure (**8a#2**) represents an isomer in which the closest contact between both rings occurs between the phosphorus in the N-heterocyclic ring and the isolated phosphorus atom in the P_3C_2 ring. This isomer is 4.2 kcal mol^{-1} less stable than the second one, and will not be considered further. The other structure (**8a#1**) is very similar to the experimental one and the calculations reproduce crucial features like the extremely long P–P bond between the rings (2.863 Å) and the leveling of the P–C bonds in the P_3C ring (P–C 1.741–1.774 Å). A strong ionic contribution to the bonding between both rings is suggested by the accumulation of substantial charges on both fragments (evaluation of the sum of NPA charges yields +0.59 for the $P(NtBu)_2(CH)_2$ and −0.59 for the $P_3(CtBu)_2$ unit), and a small value (0.38) of the Wiberg bond index for the central P–P bond, which is much lower than the values calculated for P_2H_4 (1.04) and the parent 2-phosphino-1,3,2-diazaphospholene **15** (0.95) at the same level of theory, implying a significantly reduced covalent bond order. A topological analysis of the electron density reveals further that the electron density at the bond critical point in **8a#1** ($\rho = 0.04$ a.u.) is also much lower than in P_2H_4 ($\rho = 0.11$ a.u.) or **15** ($\rho = 0.11$ a.u.). Comparison of calculated nucleus independent chemical shift (NICS) values for **8a#1** (NICS(0) = −10.0/−7.9 for the PN_2C_2/P_3C_2 rings; NICS(1) values are included in the Supporting Information) with those of the isolated cation ($[(CH)_2(N\text{-}tBu)_2P]^+$, NICS(0) = −12.1) and anion ($[P_3(C\text{-}tBu)_2]^-$, NICS(0) = −9.6; note that for the parent $P_3C_2H_2$ −13.0 was reported[12]), respectively, indicates that the perturbation of the π-electron systems is rather small, and that both rings retain appreciable aromatic character.

The ^{31}P CP-MAS spectrum of solid **8b** (Figure 4) displays twice as many spinning sideband systems as observed for **8a**, which suggests the presence of two crystallographically independent molecules; the same phenomenon had also been observed for some *P*-phospholyldiazaphospholenes

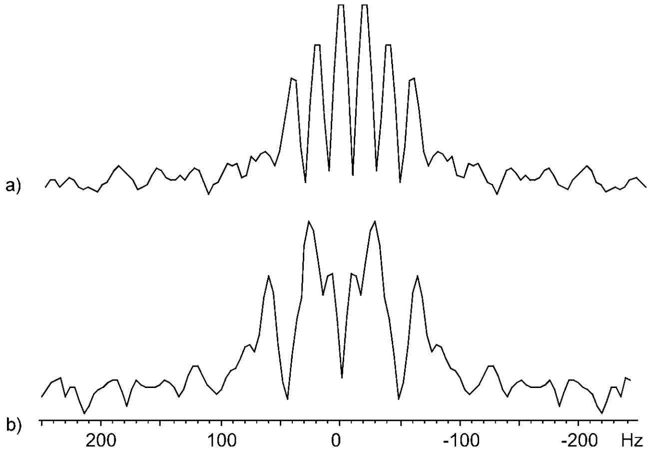


Figure 4. *F*1 slices through the symmetrized 2D *J*-resolved ^{31}P CP-MAS spectrum of **8b** showing the multiplets attributable to the diazaphospholene phosphorus atom in the two crystallographically independent specimens observed. The multiplet structure is due to homonuclear J_{PP} coupling. a) Signal at $\delta = 198.9$; $J = 39$ Hz (t), 20 Hz (d); b) signal at $\delta = 203.7$; $J = 40$ Hz (t), 48 Hz (d).

(**5**).[10] The signals of the ^{31}P nuclei in the P_2 unit of the triphosphole rings of both specimens appear as strongly overlapping pairs of doublets ($^1J_{PP} = 450$ Hz) with chemical shifts between $\delta = 236$ and 245 ppm, and the isolated phosphorus atoms in the same ring give rise to a single resonance at $\delta_{iso} = 288$ ppm; all chemical shifts are slightly larger than in **8a** but match those of ionic triphospholides ($\delta_{A2} = 252$–255, $\delta_M = 266$–271 ppm[22]). The phosphorus atoms in the N-heterocycles of both specimens give rise to two spinning sideband manifolds with chemical shifts ($\delta = 203.7$ and 198.9 ppm) that are much larger than in **8a**, but match typical values for cations in genuine diazaphospholenium salts.[19] As in the case of **8a**, smaller homonuclear couplings can be traced in a *J*-resolved 2D-NMR spectrum (see Supporting Information). Analysis of *F*1 slices through the signals of the phosphorus atom in the N-heterocyclic ring in this spectrum (Figure 4) reveals that both resonances appear as doublets of triplets, thus indicating scalar coupling to all three phosphorus nuclei in the second ring. As the magnitudes of all couplings are still smaller than the values of $^1J_{PP}$ in **5**,[10] the closest P–P distance between phosphorus atoms in different rings of **8b** is presumably still beyond the range of 2.35–2.70 Å observed for **5**.

Solution $^{31}P\{^1H\}$ NMR spectra of **8b** display, at all temperatures between −80 and +90 °C, a single set of three signals with relative intensities of 1:2:1, which show no sign of dynamically induced decoalescence down to −80 °C. A temperature-dependent variation is, however, still visible in the presence of a remarkable change in the coupling pattern: whereas the observed signals at low temperature show the characteristic splittings of a single AM_2X spin system with finite couplings between all different sites, the splitting arising from coupling between nuclei in different rings broaden and finally collapse when the temperature rises, so that in the high-temperature limit the spectrum decomposes into separate AM_2- and X-type subspectra (Figure 5).

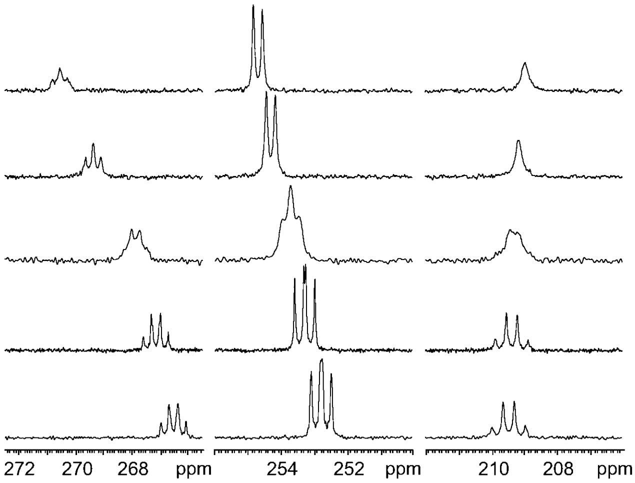


Figure 5. Expansions of the $^{31}P\{^1H\}$ NMR spectra of a [D$_8$]toluene solution of **8b** recorded at (from top to bottom) 363, 323, 273, 243, 213 K. The spectrum at lowest temperature corresponds to an AM_2X spin system with δ_A 266.5, δ_M 252.8, δ_X 209.4, $J_{AM} = 46$ Hz, $J_{AX} = 54$ Hz, $J_{MX} = 55$ Hz.

The close coincidence of chemical shifts and coupling patterns in solid-state and solution ^{31}P NMR spectra of **8b** suggests that the molecular structure in both phases is quite similar, whereas the conservation of the AM_2X-type pattern at low temperature in solution contrasts the dynamic behavior of **8a** and suggests that the molecular structures of **8a** and **8b** differ. Based on the observed chemical shift and coupling pattern, we propose to describe the solution structure of **8b** by a static C_s-symmetric arrangement of the diazaphospholene and triphosphole fragments. Because both the size of observed J_{PP} couplings and the calculations on the model compound **8H** rule out both rings of **8b** being connected by a strong covalent P–P or P–C bond, we explain the presence of scalar couplings of similar size between the diazaphospholene phosphorus atom and all three remote phosphorus atoms in the P_3C_2 ring as a consequence of through-space interactions, which requires that all coupled pairs of spins are sufficiently close to each other. This condition is fulfilled if **8b** exists like the *P*-phospholyl derivatives **5**[10] as a polarized contact ion pair in which the phosphorus atom in the N-heterocycle resides above the phosphole ring. Adopting this description allows the explanation of the collapse of the coupling between phosphorus atoms in different rings that occurs at elevated temperature in solution (Figure 5) as a consequence of the onset of intermolecular exchange of cation and anion units between different ion pairs.[28]

Although we have not yet succeeded in validating the constitution of **8b** by a single-crystal X-ray diffraction study, we were able to support the proposed structure from computational studies on the model compound **8b′** which differs from **8b** by formal replacement of *N*-mesityl by dmp substituents (dmp = 2,6-dimethylphenyl). Various energy optimization runs carried out at the B3LYP/6-31+G* level of theory and using different starting geometries allowed the location of a single minimum structure, which indeed exhibits the expected characteristics of an ion pair consisting of a diazaphospholenium cation and a triphospholide anion (Figure 6). The planar rings in both fragments are appreciably tilted relative to each other (interplanar angle 64°). The phosphorus atom of the diazaphospholene moiety (P1) resides above the P_3C_2 pentagon, and is thus in rather close proximity to all three phosphorus atoms in the other ring, with the distances to the atoms in the P_2 unit (P1–P2 3.208, P1–P3 3.225 Å) being somewhat shorter than that involving the isolated one (P1–P4 3.648 Å). The separation between both rings is not only still larger than in **8a** or in **5**,[10] but **8b′** also lacks a unique P–P interaction that may be identified as the backbone of a P–P bonded molecular structure. Instead, the observation of essentially identical P1–P2 and P1–P3 distances means the structure resembles the transition state for the 1,2-shift of the stannyl substituent in **14**,[20] and is best described in terms of a formal η^2-bonding situation. Although **8b′** exhibits C_1 symmetry, it is clearly evident that small librational motions (which require significantly lower activation energy than a 1,2-shift of the diazaphospholene unit in a P–P bonded structure) suffice to introduce ef-

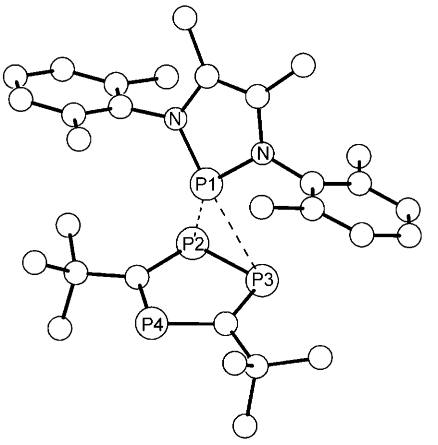


Figure 6. Representation of the molecular structure of **8b′** computed at the B3LYP/6-31+G* level of theory. Hydrogen atoms have been omitted for clarity. Relevant bond lengths are discussed in the text.

fective C_s symmetry, and allow the rationalization of the observation of an AM_2X-type pattern in the solution ^{31}P NMR spectra.

The evaluation of the sum of NPA charges for each fragment of **8b′** (+0.57/−0.57 for the $P(Ndmp)_2(CMe)_2$ and $P_3(C\mathit{t}Bu)_2$ units) gives similar results to those obtained for **8a#1** at the same level of theory, but the still lower WBI values associated with the bonding between phosphorus atoms in different rings (WBI = 0.18 (P1–P2), 0.15 (P1–P3)) indicate that the covalent interactions are even weaker than in **8a#1**. The same conclusion is also reached if one compares the electron density at the bond critical points connecting the phosphorus atoms in different rings ($\rho = 0.02/0.02$ for the P1–P2/P1–P3 bond paths vs. 0.04 for the P–P bond in **8a#1**). A comparison of NICS values (NICS(0) = −8.7/−11.5 for the PN_2C_2/P_3C_2 rings) with those of the isolated cation ($[(CMe)_2(N\text{-}dmp)_2P]^+$, NICS(0) = −10.3) and anion ($[P_3(C\text{-}\mathit{t}Bu)_2]^-$, NICS(0) = −9.6) gives atypical results, as the value for the perturbed π-system in the P_3C_2 ring of the ion pair **8b′** is even more negative than in the unperturbed triphospholide $[P_3(C{-}\mathit{t}Bu)_2]^-$, presumably reflecting the influence of the aromatic rings in the dmp substituents of the cation fragment in **8b′** rather than a real change in the electron distribution. Apart from this effect, the NICS values attest to the fact that, as for **8a#1**, both rings retain their aromatic character.

In summary, the computational studies support a description of **8b′** as an ion pair with a predominantly electrostatic interaction between the diazaphospholenium cation and triphospholide anion unit. It should be noted, however, that the nearly complete collapse of the covalent bonding interaction is not exclusively attributable to increased anion aromaticity. Comparison of the computed molecular structures of **8b′** with those of **8a#1** and the model compound **8H** indicate rather that the avoidance of unfavorable steric interaction between bulky substituents in both fragments, and the inductive (hyperconjugative) stabilization of the cation by the methyl substituents in 4,5-position, are also of importance.

Conclusion

We have demonstrated that formal CH versus P replacement in the phospholyl moiety of a *P*-phospholyl-1,3,2-diazaphospholene may further increase the ionic polarization of the homonuclear P–P bond connecting both rings. This effect is evidenced in the 1,2,4-triphospholyl derivatives **8a**,**b** by pronounced lengthening of the P–P bond, the occurrence of unusual coupling patterns between phosphorus atoms in different rings, and the scrambling of triphospholide moieties between individual molecules in solution. Although these findings follow computational predictions, which suggest relating the observed trend to the electronic stabilization of the ionic fragments in model compounds, the substantial influence of substituent effects on the computed molecular structures leads to the conclusion that the actual molecular structures arise from an interplay of both electronic and steric factors. The diazaphospholeniumtriphospholides show, in this respect, similar characteristics to frustrated Lewis pairs,[29] in which formation of a strong covalent donor–acceptor bond is prohibited mainly due to steric hindrance, and it may on these grounds be anticipated that **8a**,**b**, likewise, display an interesting reactivity towards small molecules. An exploration of this chemistry is currently in progress.

Experimental Section

General remarks: All manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques. Solvents were dried by standard procedures unless otherwise mentioned. NMR spectra were recorded on a Bruker Avance 400 spectrometer (^{1}H: 400.1 MHz, ^{13}C: 100.5 MHz, ^{31}P: 161.9 MHz) at 303 K unless mentioned otherwise; chemical shifts are referenced to external TMS (^{1}H,^{13}C) or 85% H_3PO_4 ($\Xi = 40.480747$ MHz, ^{31}P). Solid-state MAS-NMR spectra were recorded with spinning speeds from 3 to 14 kHz. Cross polarization with a ramp-shaped contact pulse with mixing times between 3 and 5 ms was used for signal enhancement in CP/MAS experiments. Coupling constants are given as absolute values. EI-MS: Varian MAT 711, 70 eV. Elemental analysis: Perkin–Elmer 24000CHN/O Analyser. Melting points were determined in sealed capillaries.

Computational studies: Geometry optimizations and energy calculations were carried out with the Gaussian03 package,[30] and the program AIM 2000[31] was used for Bader analysis of electron densities. All molecular structures were first optimized at the B3LYP/3–21G(*) level and then reoptimized at the B3LYP/6–311+G** level of theory. Harmonic frequency calculations served to identify the structures as local minima or transition states on the energy hypersurface, and to compute standard Gibbs free energies. To prove the accuracy of the methods used, CBS-QB3 and MP2 calculations have been performed. For visualization, the Molden program[32] was applied.

1,3-Di-*tert*-butyl-2-(3,5-di-*tert*-butyl-1,2,4-triphospholyl)-1,3,2-diazaphospholene (8a): 1,3-Di-*tert*-butyl-2-chloro-1,3,2-diazaphospholene (235 mg, 1 mmol) and sodium-3,5-di-*tert*-butyl-1,2,4-triphospholide (398 mg, 1 mmol) were dissolved in anhydrous THF (5 mL) and the solution was stirred for 1 h. The solvent was evaporated under vacuum and the residue suspended in anhydrous toluene (15 mL), filtered and the filtrate again evaporated to dryness. The residue was dissolved in a mixture of hexane (3 mL) and THF (2 mL). Storing the solution at −20 °C produced a yellow crystalline precipitate of **8a**, which was collected by filtration and dried in vacuum. Yield: 196 mg (48 %); m.p. 226 °C; ^{1}H NMR (C_6D_6): δ = 6.24 (s, 2H; N-C*H*), 1.97 (s, 18H; C*H*$_3$), 0.97 ppm (d, $^4J_{PH}$ = 1.8 Hz, 18H; C*H*$_3$); ^{13}C{^{1}H} NMR (C_6D_6; quaternary carbon atoms in the triphosphole ring could not be identified unambiguously due to poor signal-to-noise ratio): δ = 112.2 (d, $^2J_{PC}$ = 9.4 Hz, N-*C*H), 56.8 (m, $^2J_{PC}$ = 7.1 Hz, *C*CH$_3$), 53.0 (d, $^2J_{PC}$ = 14.5 Hz, *C*), 37.3 (dd, $^3J_{PC}$ = 10.6 Hz, 5.2 Hz, C*C*H$_3$), 30.2 ppm (d, $^3J_{PC}$ = 9.8 Hz, NC*C*H$_3$); ^{31}P{^{1}H} NMR (C_6D_6): δ = 279.6 (t, $^2J_{PP}$ = 45 Hz), 220.8 (d, $^2J_{PP}$ = 45 Hz); 159.2 ppm (s, N$_2$*P*); elemental analysis calcd (%) for $C_{20}H_{38}N_2P_4$ (440.43): C 55.81, H 8.90, N 6.51; found: C 54.93, H 8.50, N 5.90.

2-(3,5-Di-*tert*-butyl-1,2,4-triphospholyl)-1,3-dimesityl-4,5-dimethyl-1,3,2-diazaphospholene (8b): 2-Chloro-1,3-dimesityl-4,5-dimethyl-1,3,2-diazaphospholene (193 mg, 0.5 mmol) and sodium-3,5-di-*tert*-butyl-1,2,4-triphospholide (199 mg, 0.5 mmol) were dissolved in anhydrous THF (5 mL). The mixture was stirred for 1 h at ambient temperature. The solvent was then removed under vacuum, the residue taken up in anhydrous toluene (15 mL), and filtered. The filtrate was again evaporated to dryness. The residue was suspended in pentane (3 mL) and filtered. Evaporation of the filtrate and drying of the residue produced **8b** (76 mg, yield 27 %) as a red solid. M.p. 229 °C; ^{1}H NMR (C_6D_6): δ = 6.81 (s, 4H; *m*-C*H*), 2,.11 (s, 6H; *p*-C*H*$_3$), 1.99 (s, 12H; *o*-C*H*$_3$); 1.59 (s, 18H; CC*H*$_3$), 1.21 ppm (d, $^4J_{PH}$ = 1.2 Hz, 6H; C*H*$_3$); ^{13}C{^{1}H} NMR (C_6D_6; quaternary carbon atoms in the triphosphole ring could not be identified unambiguously due to poor signal-to-noise ratio): δ = 139.4 (s, *p*-*C*), 135.0 (d, $^3J_{PC}$ = 3.4 Hz, *o*-*C*), 133.1 (d, $^2J_{PC}$ = 6.9 Hz, N-*C*), 133.0 (d, $^2J_{PC}$ = 5.4 Hz, *i*-*C*), 130.2 (s, *m*-*C*H), 37.5 (dt, $^2J_{PC}$ = 10.6 Hz, $^2J_{PC}$ = 5.3 Hz, *C*CH$_3$); 25.8 (s, *p*-*C*H$_3$), 21.0 (s, *o*-*C*H$_3$), 18.7 (d, $^3J_{PC}$ = 1.5 Hz, NC-*C*H$_3$), 11.6 ppm (d, $^3J_{PC}$ = 3.8 Hz, C*C*H$_3$); ^{31}P{^{1}H} NMR (C_6D_6): δ = 268.6 (br t, $^2J_{PP}$ = 48 Hz, C$_2$P), 255.1 (br d, $^2J_{PP}$ = 48 Hz, *P*$_2$), 211.0 ppm (br s, N$_2$*P*); elemental analysis calcd (%) for $C_{32}H_{46}N_2P_4$ (582.63): C 65.97, H 7.96, N 4.81; found: C 65.20, H 7.9, N 4.3.

Crystal structure determination of 8a: Crystallographic data were collected on a Bruker-Nonius Kappa CCD diffractometer at 100(2) K with Mo$_{K\alpha}$ radiation (λ = 0.71073 Å). Direct Methods (SHELXS-97[33]) were used for structure solution and refinement (SHELXL-97,[34] full-matrix least-squares on F^2). Hydrogen atoms were refined using a riding model. Data: orange crystals, $C_{20}H_{38}N_2P_4$, M_r = 430.40; crystal size 0.25 × 0.30 × 0.30 mm; orthorhombic; space group $Pna2_1$ (No. 33), a = 20.6178(4), b = 10.0657(2), c = 12.0430(2) Å; V = 2499.3(1) Å^3; Z = 4; ρ_{calcd} = 1.144 Mg m^{-3}; $F(000)$ = 928; μ = 0,31 mm^{-1}, numerical absorption correction (HABITUS[35]), 36556 reflections ($2\theta_{max}$ = 56.6°), 6194 unique [R_{int} = 0.066], 248 parameters, 1 restraint, $R1$ [$I > 4\sigma(I)$] = 0.036, $wR2$ (all data) = 0.078, Flack x parameter = −0.06(6), largest diff. peak and hole 0.20/−0.19 e A^{-3}.

CCDC-741939 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

The Deutsche Forschungsgemeinschaft (Grant Gu415/13-1) and the DFG-HAS travel grant are acknowledged for funding. We also thank COST action CM0802 "PhoSciNet" for supporting this work.

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Received: October 22, 2009