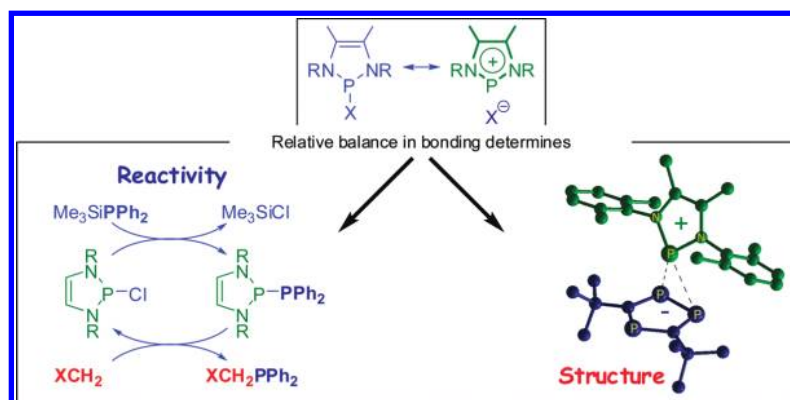# Diazaphospholenes: *N*-Heterocyclic Phosphines between Molecules and Lewis Pairs

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CONSPECTUS

The interest in geometrically distorted or electronically polarized molecules is often motivated by the realization that unusual structures can engender unprecedented physical or chemical properties. 1,3,2-Diazaphospholenes are *N*-heterocyclic phosphines (NHPs) that have ring structures similar to *N*-heterocyclic carbenes (NHCs). Although NHPs were initially mainly of interest as precursors for carbene-analogous phosphenium cations, it was noted that they exhibit quite peculiar structural features and remarkable chemical behavior on their own. In this Account, we discuss both structure and chemistry in connection with the special bonding situation that is characterized by significant $n(N)-\sigma^*(P-X)$ hyperconjugation and induces a strong ionic polarization of the P−X bonds.

This induced polarization is surprisingly maintained even when P and X have similar or like electronegativities (for example, X = H, P) and offers the possibility to design compounds with polarized homonuclear bonds. An exemption from the general pattern was only noted for some *P*-amino-NHPs in which reverse hyperconjugation weakens endocyclic P−N bonds and was predicted to facilitate ring fragmentation and formation of phosphinidenes. An important corollary of the P−X bond polarization in NHPs is a unique bond lengthening, which not only can be fine-tuned by adjusting intramolecular steric and electronic interactions but also responds to intermolecular influences and solvent effects.

Insight from crystallographic, spectroscopic, and computational studies allows the development of concepts for controlled manipulation of the bonding, up to a point where P−X bonds are dominated by electrostatic interactions and species behave as Lewis pairs rather than covalent molecules. An appealing aspect lies in the fact that this P−X bond polarization induces reactivities that have hardly any precedence in phosphine chemistry. Examples include (i) reactions of *P*-hydrogen-substituted NHPs as hydride transfer reagents, (ii) metatheses and additions to multiple bonds (diphosphination) of phosphino-NHPs, which can be used to catalyze P−C cross-coupling reactions and to synthesize 1,2-bisphosphine ligands, (iii) cyclopentadienyl (Cp) transfer reactions of *P*-Cp-NHPs, and (iv) metal insertion into the P−X bonds of *P*-halogeno-NHPs. In many aspects, these reactions have potentially useful mechanistic or synthetic implications, and their future exploitation might help to convert NHPs from academically interesting species into useful reagents.

Introduction

The discovery of *N*-heterocyclic carbenes **I** (E = C, Chart 1) in the early 1990s[1] was a landmark and set off a boom in the investigation of stable *N*-heterocyclic carbenes (NHCs), their metal complexes, and applications of ligands and complexes in synthesis and catalysis.[2] In the wake of this development, also a quest for isoelectronic analogues of NHCs with elements other than carbon was initiated or, where such species were already known, intensified and renewed. To date, carbene analogues **I** with elements from groups 13−16 are known, including congeners with heavier group 14 elements (E = Si, Ge, Sn), monoanions and monocations with group 13 (E = B, Ga) and group 15 elements (E = N, P, As, Sb), respectively, and dicationic species centered around the group 16 elements sulfur and selenium.[3,4]

In the context of the exploration of phosphenium cations **I** (E = P), also neutral *N*-heterocyclic *P*-chlorophosphines **II** (X = Cl) caught attention. These compounds had come into play as synthetic precursors for the cations, but it had been noted from the beginning that they displayed by themselves unique structural features like unusually long P−Cl bonds;[5] in fact, one compound was even addressed as ionic species, which had supposedly formed via spontaneous P−Cl bond heterolysis.[6] Although this hypothesis became questionable in the light of more detailed studies, the original idea, that the high stability of the cyclic π-electron system in cations **I** (E = P) can act as driving force to enhance P−Cl bond ionicity in chlorophosphines **II** (X = Cl), turned up again as a key motif in the representation of the bonding situation in terms of resonance between covalent (**IIa**) and ionic canonical structures (**IIb**).[7] In exploring the chemistry of these compounds, we found that a similar situation applies also to type **II** molecules with phosphino (X = PR₂),[8] hydrogen (X = H),[9] or cyclopentadienyl substituents (X = C₅R₅)[10] where the P−X bonds connect now two atoms of similar electronegativity. Inclusion of a canonical structure **IIb** implies thus polarization of a bond that is intrinsically nonpolar and relates these compounds to polarized organic molecules, which may easily undergo heterolytic CC bond cleavage.[11] As it turned out, this bonding situation not only affects the structural properties of derivatives **II** but

CHART 1. Generic Molecular Structures of NHC Analogues **I** and *N*-Heterocyclic Phosphines **II**
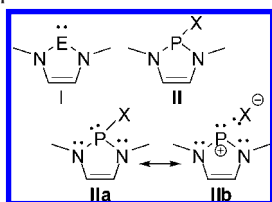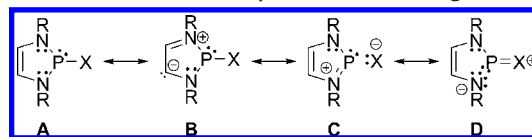

CHART 2. Valence Bond Description of the Bonding in NHPs **II**[a]

[a] Mirror images of structures **B**−**D** were omitted.

induces indeed a chemical reactivity that is in many aspects unprecedented for phosphines. This Account will reflect on our experimental and computational studies on structural aspects of *N*-heterocyclic phosphines **II** and the connection between their special bonding situation and unique chemical reactivity.

Understanding Structure and Bonding: Computational and Experimental Studies

Computational studies on different NHPs **II** (with X = halogen, H, PR₂, NR₂) were performed using mainly DFT or MP2 methods. Analysis of calculated electron densities or wave functions by the NBO and NRT formalism revealed that the P−X bonding is influenced by competition between hyperconjugation interactions that can be described by resonance between canonical structures **A**−**D** (Chart 2; **D** does not apply to X = H).[7−9,12] The situation in *P*-halogen, *P*-hydrogen, and *P*-phosphino derivatives is dominated by the n(N)−σ*-(P−X) interaction (higher contribution of ionic canonical structure **C**), which reduces covalent bond orders and strengthens the charge separation P(δ^+)−X(δ^-), thus implying an increased bond ionicity.[7−9] This effect is particularly strong in *P*-halogen derivatives, which exhibit already a pronounced intrinsic bond polarity, and provided a key argument in describing these compounds as Lewis acid−base complexes with a "dative" (or highly polarized covalent) bond.[7] A similar depiction (albeit with higher covalent contributions) was also proposed for *P*-phospholyl NHPs[13] and can be considered as special manifestation of a concept lately proposed by Macdonald et al.[14] who related the comparatively low Lewis acidity of all amino-phosphenium ions to the fact that formation of a Lewis base adduct disrupts the NPN−π-delocalization and is therefore energetically less favorable than for other types of phosphenium ions. The assessment of *P*-phosphino NHPs as donor−acceptor complexes highlights further a close relationship to cationic phosphenium−phosphine complexes whose chemistry has recently been rediscovered and further developed by Burford et al.[15]

In contrast to the situation just described, the characteristics of exocyclic and endocyclic P−N bonds in *P*-amino-NHPs seem to be determined by a balance between n(N)−σ*(P−X) (canonical structure **C**) and n(X)−σ*(P−N) hyperconjugation (canonical structure **D**).[12] In accord with this view, crystal struc-

TABLE 1. Typical Ranges of Endocyclic and P−X Bond Distances (in Å) in NHP Derivatives of Type **II**

X	no. of structures	P−N[a]	N−C[a]	C−C[a]	P−X[a]	refs
—[b]	18	1.66−1.69	1.36−1.39	1.34−1.38		5, 7, 19
F	1				0.165	7
Cl	12				2.24−2.70	5, 7, 19
Br	2	1.64−1.67	1.38−1.43[c]	1.33−1.35	2.62−2.95	20, 21
I	1				3.43	20
N$_3$	1				1.86	22
H	2	1.69−1.72	1.41−1.42	1.32−1.33	1.48−1.51	9, 23
PR$_2$[d]	12	1.70−1.74	1.39−1.42	1.32−1.34	2.31−2.70	8, 13, 23, 25
P$_3$CR$_2$[e]	1	1.67−1.68	1.38−1.39	1.32	2.79	26
NR$_2$[f]	6	1.70−1.73	1.40−1.41	1.32−1.33	1.67−1.81	12, 16
C$_5$R$_5$	2	1.71−1.74	1.40−1.42	1.32−1.33	1.92−1.95	10

[a] Standard bond distances (in Å): P−N = 1.64; C−N = 1.36; C=C = 1.32; P−C = 1.86; P−Cl = 2.01; P−P = 2.21. [b] Values of diazaphospholenium cations for comparison. [c] Maximum bond length 1.41 Å if 4,5-dimethyl substituted derivatives are excluded. [d] Including phospholyl-substituted derivatives. [e] P$_3$CR$_2$ = 3,5-di-*t*-butyl-1,2,4-triphospholyl. [f] Including pyrido-annelated derivatives.

ture studies revealed that the exocyclic P−N bonds of some monocyclic or pyrido-annulated P-amino-NHPs[12,16] are even shorter than the endocyclic ones. Upon interpretation of this finding as relative weakening of the *endo*cyclic P−N bonds, it was proposed that the effect might facilitate [4 + 1]-cycloreversion of the heterocyclic framework to give a phosphinidene and a diimine.[17,18] Computational studies indicated that such a reaction is highly endothermic for molecules with isolated rings but becomes energetically more accessible for annulated heterocycles where the fragments can gain additional stabilization from aromatization of the remaining ring and might then provide a viable approach to generate free phosphinidenes.[17]

An important corollary of the bonding situation in NHPs **II** are specific structural distortions that are readily identified from examination of computed geometries of isolated molecules in the gas phase and from X-ray diffraction data. Comprehensive studies have been performed for *P*-halogen, *P*-amino, and *P*-phosphino derivatives; in addition, some *P*-hydrogen and *P*-cyclopentadienyl derivatives were studied (Table 1). The heterocyclic rings of all specimens display more or less folded envelope conformations and can be grouped into two sets each of which exhibits a rather narrow distribution of bond lengths. *P*-Halogeno and *P*-azido derivatives make up the first group and have slightly shorter C−C but longer C−N bonds than 1,3,2-diazaphospholenium cations, which exhibit the strongest π-delocalization and were accordingly recognized as aromatic molecules.[27] The second group includes all other compounds and is distinguished by a further decrease in C−C and also a small increase in P−N bond lengths. Although interpretation of X-ray data using quantitative structure correlation was not possible,[19] the variations in computed molecular structures correlate with an increasing π-electron localization in the neutral NHP derivatives.

The most prominent structural feature of NHPs is without doubt a substantial lengthening of the P−X (X = H, PR$_2$, C$_5$R$_5$) bonds with respect to standard single bond distances, which becomes evident in both experimentally determined (Table 1) and computed molecular structures. Particularly large effects are observable in *P*-halogeno-NHPs (e.g., P−Cl = 2.24−2.70 Å)[19] and, in particular, *P*-phospholyl-NHPs (P−P = 2.35−2.70 Å)[8,13] where the distances can even exceed those in compounds with "one-electron bonds" (2.43−2.63 Å), which formally connect two phosphorus atoms by a single bonding electron.[28] Structure correlation analysis revealed that changes in P−Cl and P−N distances in *P*-chloro-NHPs exhibit an inverse relationship (Figure 1) but are uncorrelated with variations in N−C and C−C distances, supporting the view that the structural distortion is related to n(N)−σ*(P−Cl) hyperconjugation[19] and a particularly strong π-stabilization of the corresponding cations.[14] Although a similar relation between P−Cl and P−N bond lengths holds also for other diaminochlorophosphines (R$_2$N)$_2$PCl, the variance and absolute values of the P−Cl distances in NHPs are much larger than those in the reference compounds and indicate thus that the P−Cl bond is "softer" (i.e., more easily polarizable).[19] Examination of structural changes in *N-t*-butyl-NHPs, **1**, featuring different *P*-halogen substituents indicated that the P−F bond was less affected by hyperconjugation[7] whereas P−Br[20,21] and P−I[20] derivatives showed even more pronounced bond lengthening (Table 1).

P-Phospholyl-NHPs exhibit unusually small P−P−C bond angles at the phosphole P atom (79−89°), which decrease when the P−P distances become longer so that P−P bond lengthening is accompanied by a shift of the NHP moiety from a peripheral position toward a point above the centroid of the phosphole ring (Figure 2). This trend was interpreted as reflect-
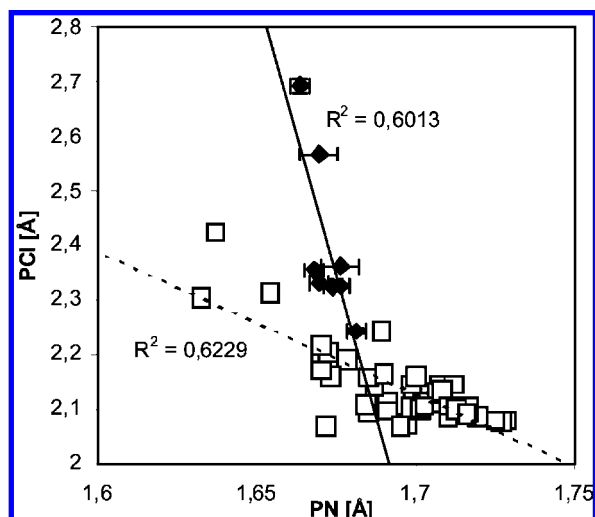
FIGURE 1. Plot of P−Cl distances (in Å) vs average P−N distances (in Å) for Cl-NHPs (◆) and all other diamino-chlorophosphines $(R_2N)_2PCl$ listed in the CSD database (□). Solid and dashed lines represent the results of linear regression analyses. Error bars at the data points denote a range of $\pm 3\sigma$ where σ is the estimated standard deviation. R^2 is the square of the correlation coefficient in the regression analysis. Reproduced with permission from ref 19. Copyright 2007 Wiley-VCH Verlag GmbH & Co. KGaA.
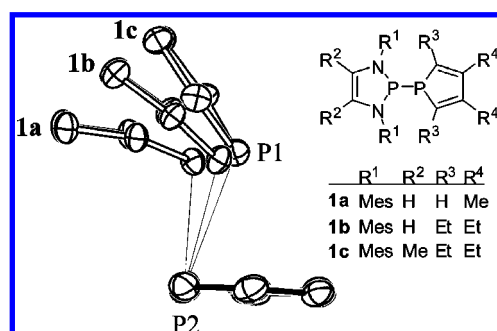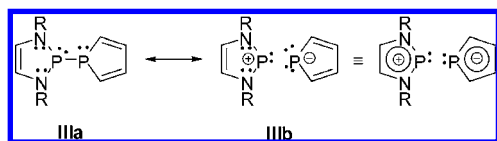

FIGURE 2. Overlay of the cyclic cores of three *P*-phospholyl-NHPs, **1a−c**. The molecular structures are arranged in a way that the phosphole rings (P2) are superimposed on each other. Substituents are omitted for clarity (structures from taken from ref 13).

CHART 3. Ionic and Covalent Canonical Structures for Phospholyl-NHPs **III**

ing an increasing bond ionicity, which puts more emphasis on an ionic canonical structure **IIIb** (Chart 3) and should enforce a closer approach of the centers of positive and negative charge in both rings. On the other hand, the finding that the bond length distribution in the phosphole rings is still closer to the structure of a conjugated diene than that of an aromatic heterocycle was taken as evidence for a still appreciable covalent character of the P−P bond.[13]

Intermolecular and Solvent Influences on P−X Bond Polarization

Examination of trends in computed and experimentally determined structural parameters of NHPs revealed that the computations reproduced structural changes induced by the influence of different P- or N-substituents but failed in a quantitative assessment of P−X distances. Large deviations were in particular noted for phospholyl-NHPs **III**,[13] where DFT calculations seemed to overestimate the P−P distances, and in *P*-halogenated derivatives,[7,20,19] where the calculated bond distances were much too short. Although part of the deviations reflect certainly the marked dependence of calculated distances on the computational model and must thus be considered a methodological artifact,[13] there was also *experimental* evidence that individual compounds showed a pronounced variation in bond distances in response to subtle crystal packing effects. The most lucid examples include a deviation as large as 4 pm between the P−P distances of crystallographically independent molecules of a *P*-phospholyl-NHP,[13] and the observation of a similar difference between the P−Cl bond lengths of a *P*-chloro-NHP and its toluene solvate.[7] An obvious explanation is that these changes reflect the action of *intermolecular* rather than *intramolecular* influences. Direct substantiation of this hypothesis was derived from a computational study of 1,3-di-*t*-butyl-2-iodo-1,3,2-diazaphospholene, **2**, where the calculated P−I bond distance of 2.852 Å for an isolated molecule in the gas phase was much shorter than the value of 3.426 Å determined by single-crystal X-ray diffraction; in contrast, a periodic plane wave geometry optimization at the same level of theory not only yielded a shortest P−I distance of 3.407 Å in good agreement with the experimental data but reproduced as well the one-dimensional array of interacting diazaphospholenium and iodide ions that had been observed in the X-ray diffraction study (Figure 3).[20] A deeper investigation revealed that the P−I bond of a single molecule tolerates large variations without a substantial rise in energy and led to the conclusion that actually observed bond lengths are controlled by the influence of both intramolecular hyperconjugation and intermolecular dipolar polarization by neighbor molecules.

The influence of solvent effects on phosphorus−halogen distances was further illustrated in case of the analogous *P*-chloro-NHP where the calculated P−Cl bond distance for a single molecule in the gas phase was found to increase continuously upon immersion in solvents of increasing polarity.[29] It has been pointed out that this solvent-induced bond polarization explains both the unique solvent dependence of
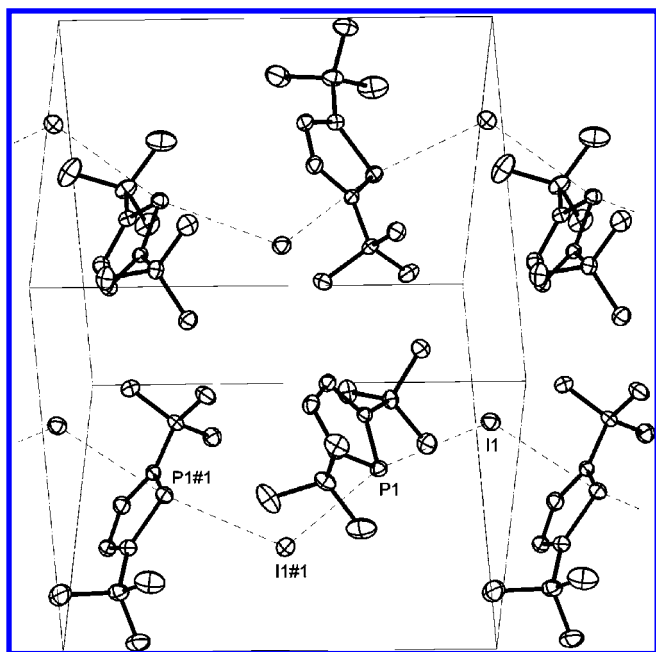
FIGURE 3. Representation of the unit cell of 1,3-di-*t*-butyl-2-iodo-1,3,2-diazaphospholene, **2**. Thermal ellipsoids were drawn at the 50% probability level, and hydrogen atoms were omitted for clarity. Interactions between NHP fragments and iodine atoms parallel to the crystallographic *b*-axis are represented as dashed lines. Selected distances (Å) and angles (deg): I(1)−P(1) = 3.426(1); I(1)−P(1)#1 = 3.558(1); P(1)−I(1)−P(1)#1 = 107.26(1); I(1)−P(1)−I(1)#2 = 164.14(2). Symmetry transformations used to generate equivalent atoms: #1, 1.5 − *x*, *y*, −0.5 + *z*; #2, 1.5 − *x*, *y*, 0.5 + *z*. Reproduced with permission from ref 20. Copyright 2009 Wiley-VCH Verlag GmbH & Co. KGaA.

NMR chemical shifts of *P*-chloro-NHPs in solution[5,7] and the solvate-induced modification of P−Cl bonds in the solid state.[29] A substantial solvent influence on P−P distances was likewise inferred for *P*-phospholyl-NHPs where it was established that the large deviations of $^1J_{PP}$ coupling constants measured in solid-state and solution NMR spectra and the marked temperature dependence of the coupling in solution are attributable to the combined effects of a temperature-dependent equilibrium between rotamers and a relaxation of P−P bond distances in solution (Figure 4).[13]

Covalent vs Dative Bonds: From Molecules to Lewis Pairs

The studies of the molecular structures of NHPs discussed so far reveal that exocyclic P−X bonds are generally much longer than normal single bonds and that in particular P−P and P−halogen bonds are highly tolerant toward distortion, responding to subtle inductive substituent effects and even to intermolecular or solvent effects. Computational studies predicted further that all P−X bonds exhibit a substantial polarity $P^{(\delta+)}-X^{(\delta-)}$ and tend to react under heterolytic rather than
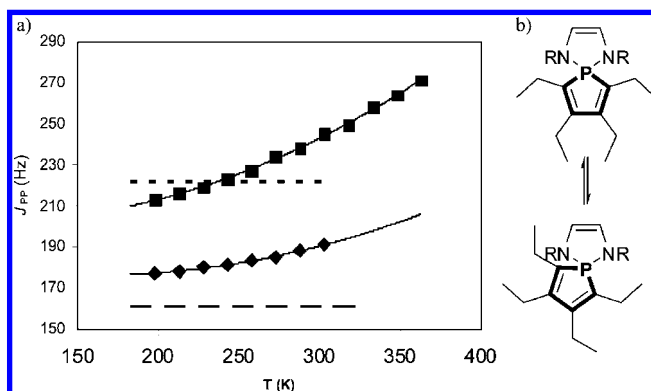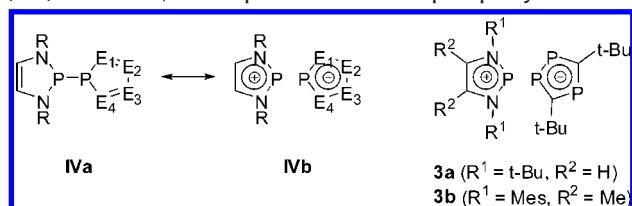

FIGURE 4. (a) Representation of $^1J_{PP}$ values for **1b** (R = Mes, ◆) and **1d** (R = DIPP, ■) derived from solution ^{31}P NMR spectra. Dashed lines denote the $^1J_{PP}$ values measured from solid-state NMR spectra, and the difference between the low-temperature limit of $^1J_{PP}$ in solution and the solid-state value was attributed to P−P bond length relaxation (data from ref 13). The variation of $^1J_{PP}$ with temperature is caused by a temperature-dependent conformational equilibrium depicted in panel b (formulas drawn as projections along the P−P bond).

homolytic cleavage even in cases where the electronegativities of P and X are similar or the same,[8,9] which is in fact in accord with the actually observed chemical behavior that will be discussed later on. The intermediate bonding situation (between genuine covalent and ionic) in phospholyl-NHPs was further highlighted by a topological analysis of the electron density, which revealed that electron densities at bond critical points are generally low, that Laplacians change with increasing bond lengthening from small negative to small positive values, and that increasing the bond lengths does not produce new bond or cage critical points but leaves the covalent interaction localized between the phosphorus atoms in both rings.[13] All these features represent typical attributes of dative (donor−acceptor) bonding as defined by R. S. Mulliken[30] and led us to picture NHPs as hybrids between covalent molecules and Lewis pairs consisting of cyclic phosphenium cations and appropriate anions and to describe the P−X bonds as dative donor−acceptor interactions rather than "normal" covalent bonds.[13]

In light of the previous remarks, the bonding situation in *P*-phospholyl derivatives is without doubt a most interesting case due to the introduction of ionic polarization into a homonuclear P−P bond, which relates them to the systems with polarized C−C bonds studied by Arnett et al.[11] Further consideration of this aspect raised the question whether it was possible to design diphosphines with even more polarized P−P bonds that are no longer governed by covalent contributions but are predominantly ionic. Starting from the concepts that the strong polarization in *P*-phospholyl NHPs benefits from aromatic stabilization in both the cation and the

CHART 4. Generic Molecular Structure of Polyphospholyl-NHPs **IV** (E_1-E_4 = P or CR^3) and Representatives of Triphospholyl-NHPs **3**

IVa   **IVb**

3a (R^1 = t-Bu, R^2 = H)
3b (R^1 = Mes, R^2 = Me)

SCHEME 1. Selected Reactions of *P*-Hydrogen-NHPs[a]

[a] R = alkyl, aryl.

anion fragment of a canonical structure **IIIb** (Chart 3) and that formal replacement of additional CH units in the phosphole ring by phosphorus atoms further enhances the aromatic stabilization in the anion fragment,[31] it was expected that polyphospholyl-substituted NHPs **IV** (Chart 4) should offer a still closer approach to true "phosphenium-phosphides".[26] The validity of this approach was endorsed by computational studies (trends in computed structural data, electron distributions, and ligand exchange reaction energies of model compounds of type **IV** indicated that the energy for charge separation declines and the P−P bond ionicity goes up with increasing number of phosphorus atoms in the phospholyl ring) and finally experimentally confirmed through the characterization of some triphospholyl-substituted NHPs **3** (Chart 4). Unique features of these derivatives include a further rise in P−P bond distances (≥2.80 Å, Figure 5), the observation of small or even vanishing $^1J_{PP}$ coupling constants, which exclude a strong covalent P−P interaction both in the solid state and in solution, and the observation of temperature-dependent NMR spectra, which reveal the occurrence of intermolecular exchange of cyclic phosphenium and triphospholide fragments in solution. All features together support a description of these species as ion pairs with a mainly electrostatic interaction and a nearly complete collapse of the covalent bond-
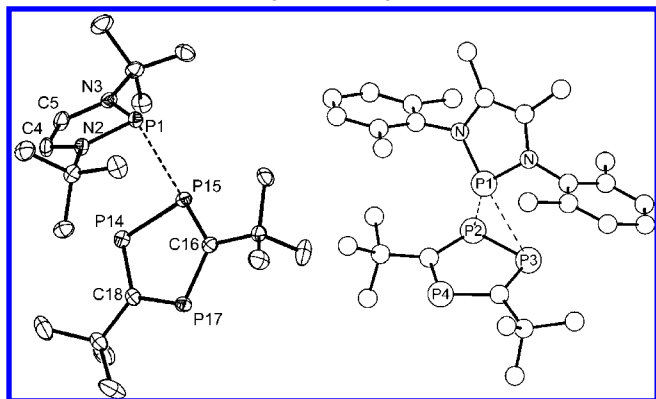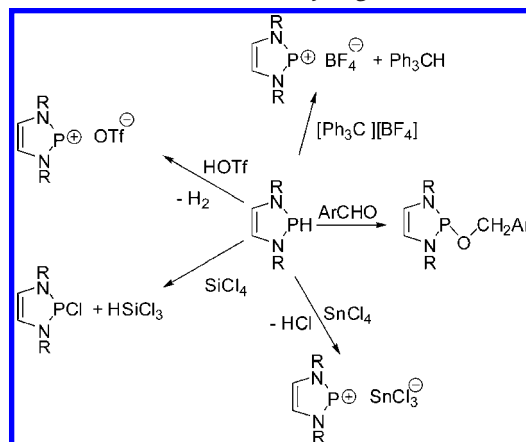
ing between the cation and anion units. A lucid illustration is provided by the computed molecular structure of **3b** (Figure 5b); however, the unusual topology, which is best described by a contact ion pair with shifted η^5-arrangement of the cation fragment with respect to the triphosphole ring, is not exclusively attributable to anion aromaticity, but steric effects and additional inductive stabilization by the methyl substituents in the cation were likewise considered important.[26]

Chemical Reactivity: "Umpolung" of Phosphorus−Hydrogen Bonds

The appeal of the special bonding situation in NHP derivatives lies in the fact that the ionic bond polarization induces not only structural distortions but implies also a unique chemical reactivity. One of the earliest manifestations of this aspect was the realization that *P*-hydrogen NHPs may react as molecular hydrides (Scheme 1) and contrast thus the normal behavior of secondary phosphines, which are weak acids.[9] Accordingly, reactions with acids produced dihydrogen and a phosphenium salt, and reaction with a triphenylcarbenium salt yielded triphenylmethane. Aldehydes and ketones did not react to give α-phosphino-carbinols as is usually observed in reactions with secondary phosphines but were reduced to phosphorodiamidites (which may also be regarded as NHP alkoxides);[9,23] this reduction is chemoselective because aldehydes and diaryl ketones are converted at much higher rates than alkyl ketones[23] and may thus be selectively reduced. Reduction of carbon tetrachloride with an equimolar amount of a *P*-hydrogen NHP was unselective and gave a mixture of chlorohydrocarbons CH_nCl_{4-n} (n = 0−3), but tetrachlorides of the heavier group-14 elements reacted via hydride/chloride metathesis to produce exclusively $EHCl_3$, which either was stable (E = Si) or decayed via reductive elimination of hydrogen chloride and chloride transfer to give phosphenium

FIGURE 5. Representation of the molecular structures of diazaphospholenium triphospholides **3a** (from X-ray diffraction data, left) and **3b** (computed structure at the B3LYP/6-31+G* level of theory, right). Hydrogen atoms have been omitted for clarity. Relevant bond distances: **3a**, P1−P15 2.793(1) Å; **3b**, P1−P2 3.208 Å, P1−P3 3.225 Å, P1−P4 3.648 Å. Reproduced with permission from ref 26. Copyright 2010 Wiley-VCH Verlag GmbH & Co. KGaA.
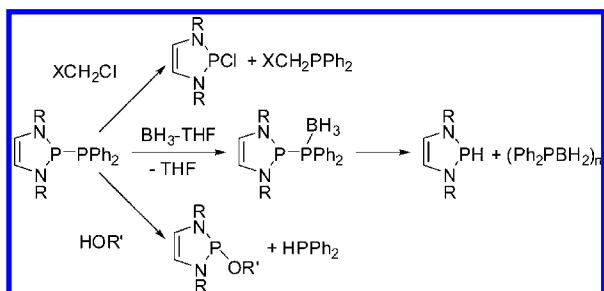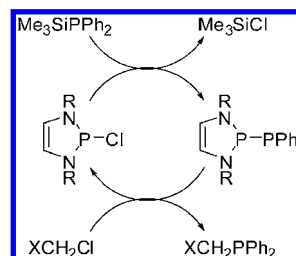
SCHEME 2. Selected Metathesis Reactions of *P*-Diphenylphosphino-NHPs[a]

[a] R = alkyl, aryl; R' = alkyl; X = alkyl, aryl, Cl.

SCHEME 3. NHP-Catalyzed Phosphorus Carbon Cross-Coupling Reaction ([a])

[a] According to ref 33.

SCHEME 4. Selected Addition Reactions of *P*-Phosphino-NHPs[a]
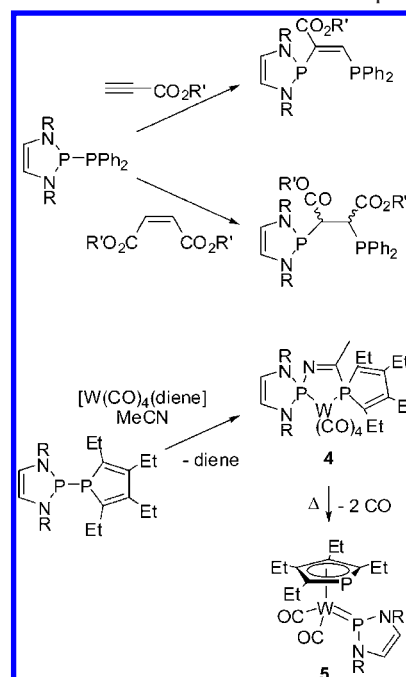

[a] R = aryl; R' = alkyl.

trichlorogermanates or -stannates, respectively (E = Ge, Sn).[23] Furthermore, $SnCl_2$ or $SnCl_3^-$ were cleanly reduced to the element. Reactions of *P*-hydrogen-NHPs with *P*-chloro-NHPs or 1,3,2-diazaphospholenium triflates allowed the first experimental detection of intermolecular exchange of a hydride, rather than a proton, between phosphine derivatives. Computational studies suggest that this reaction proceeds via a symmetrical P···H···P bridged transition state featuring a three-center, two-electron bond, which can be considered isolobal to hydride-bridged $[B_2H_7]^-$ and emphasize thus the pronounced hydride character of *P*-hydrogen-substituted NHPs.[23] The preference for P···H···P over P···P-bonded adducts was explained by considering the low electrophilicity of 1,3,2-diazaphospholenium cations, which disfavors orbital-controlled reactions (formation of a dative P−P bond) over charge-controlled reactions (formation of a H-bridged adduct with a higher degree of ionic bonding) and makes these species thus harder Lewis acids than other phosphenium ions.[23,29] It should be mentioned that structural evidence for a P···H···P interaction had previously been reported.[32]

P−P Bond Activation and Cleavage

The polarized P−P bonds render *P*-phosphino-NHPs highly active reactants for various metathesis and addition reactions under very mild conditions. Metathesis occurred upon treatment with alcohols or chloroalkanes (Scheme 2)[8,33] or with transition metal halide complexes.[34] An interesting process was found in a two-step reaction, which combined the generation of a *P*-phosphino-NHP via coupling of a *P*-chloro derivative with diphenyl(trimethylsilyl)phosphine and subsequent metathesis with chloroalkanes to produce high yields of *P*-alkyl-diphenylphosphines. As the chloro-NHP is regenerated in the second reaction step and may be recycled, it can be merely used as catalyst (Scheme 3).[33] It was pointed out that P−P bond polarization is indeed crucial for the overall acceleration of the P−C cross coupling. Furthermore, because the catalysis relies on the high stability of *N*-heterocyclic phosphe-

nium cations, the reaction is related to the ligand exchange on phosphenium centers first reported by Burford et al.[15] and represents the first catalytic transformation that depends on the electrophilic rather than the nucleophilic character of an organophosphorus compound.

Electron-poor alkenes and alkynes with one or more electron-withdrawing nitrile or ester substituent react with *P*-phosphino-NHPs via addition ("phosphinyl-phosphination") to the multiple bond (Scheme 4), thus offering one-step access to unsymmetrical bis-phosphines from simple organic precursors.[8,25,34,35] Whereas additions to alkynes occur more easily and were also observed for other types of diphosphines,[36] addition to alkenes requires a highly reactive P−P bond and seems to be specific for *P*-phosphino-NHPs.[25] Unsymmetrically substituted alkenes or alkynes yield a single regioisomer carrying the *P*-phosphino substituent of the NHP at the more electrophilic carbon atom. Additions to

alkynes proceed also stereospecifically to give exclusively Z-ethylene-bis-phosphines,[24,35] whereas the stereochemistry of the addition to alkenes depends on the substrate. Thus, cyclic maleic imide gave a single product with *cis* configuration of the phosphino groups, whereas acyclic fumaric or maleic esters produced a mixture of *cis*- and *trans*-configured addition products both of which were, however, converted into a single chelate complex with the stereochemically more favorable *trans* configuration upon subsequent reaction with (cyclooctadiene)palladium dichloride.[25] The stereochemical preferences were rationalized by assuming that additions to alkenes proceed via transient carbanions, which undergo epimerization unless their configuration is fixed by a rigid ring structure.

An appealing reaction between *P*-phosphino-NHPs, acetonitrile, and [W(CO)$_4$(cyclooctadiene)] proceeded via addition to the nitrile triple bond and formation of a chelate complex with a PCNP backbone (Scheme 4).[35] It has been shown that both activation of the nitrile by metal coordination and activation of the P−P bond by ionic polarization are crucial for the formation of the chelate complex **4**[34] and that the nitrile may again be liberated in a thermolysis reaction, which produced a phosphenium-phospholide complex **5**.[25,34]

The cause for the high P−P bond reactivity of *P*-phosphino-NHPs becomes evident in the reaction of a thermally stable derivative with borane−THF to give a transient, spectroscopically detectable phosphine−borane complex, which then decayed below room temperature via P−P bond cleavage to furnish a *P*-hydrogen-NHP and oligomeric (Ph$_2$PBH$_2$)$_n$ (Scheme 2).[37] The increased P−P bond lability in the transient complex was attributed to the fact that coordination of an electrophile to the PPh$_2$ group of the starting diphosphine improves the stabilization of negative charge and promotes thus a further increase in P−P bond ionicity. This effect in turn facilitates subsequent bond cleavage and may thus be considered to invoke an "autocatalytic" activation mechanism.[37]
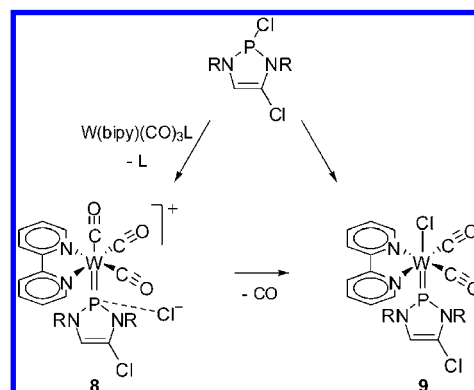
Diverse Reactivity of *P*-Cyclopentadienyl-NHPs

P-Cyclopentadienyl-NHPs were found to undergo, like *P*-phospholyl-derivatives, metatheses with transition metal chlorides to produce metal cyclopentadienyls and *P*-chloro-NHPs.[10] Alternatively, deprotonation of the C$_5$H$_5$-substituted derivative **6** gave a lithium cyclopentadienyl complex **7**, which reacted further with iron dichloride to produce a 1,1′-bis-NHP-ferrocene (Scheme 5). The high P−C bond reactivity in **6** is in accord with the presence of a substantially lengthened P−C bond (1.95 Å), whereas **7** contains a normal single bond (P−C

SCHEME 5. Reactivity of a *P*-Cyclopentadienyl-NHP[a]
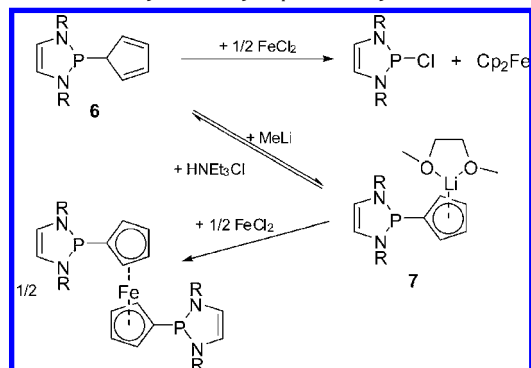
[a] R = Mes.

SCHEME 6. Metal Insertion Reaction of a *P*-Chloro-NHP[a]

[a] R = Mes, L = MeCN.

1.79 Å) that does not imply any special reactivity. Cp transfer reactions have not been reported for conventional cyclopentadienyl phosphines, and it appears that the unique reactivity of **6** owes once again to the prepolarization of the P−C bond, which should facilitate separation of the cationic diazaphospholenium and anionic cyclopentadienyl fragments during a metathesis reaction.

Metal Insertion into a Phosphorus−Chlorine Bond

Although the reactivity of the phosphorus−halogen bonds is, as a consequence of their natural polarity, sufficient to make *P*-halogeno-phosphines valuable synthetic reagents, the extra polarization in *P*-halogeno-NHPs is still the source of some peculiar chemistry. This is illustrated by the reaction of a *P*-chloro-NHP with [W(bipy)(CO)$_3$(MeCN)] shown in Scheme 6, which does not proceed as simple ligand replacement to give a phosphine complex but yields an isolable neutral phosphenium complex **9** via a spectroscopically detectable intermediate **8**.[38] The reaction is remarkable because the final product represents a rare halide complex of a formally zero-valent transition metal, the conversion of the starting ligand into the complexes **8** and **9** gives mechanistic insight into the inser-

tion of a metal atom into a P—Cl bond, and, finally, the observation of spontaneous P—Cl heterolysis without assistance of a Lewis acid contradicts a common reaction pattern of coordinated chlorophosphines, which are normally reluctant to release a chloride. Both the unusual reaction pathway and the possibility to observe the reaction intermediate **8** are again to a large extent attributable to the strong prepolarization of the P—Cl bond in the starting chloro-NHP. A similar formation of a cation-captured Pd(0)-bromide was recently also observed during the reaction of a *P*-bromo-NHP with tetrakis-triphenylphosphine palladium(0).[21]

Conclusions

It has been illustrated that *N*-heterocyclic phosphines (NHPs) exhibit a peculiar bonding situation, which is produced by an interplay of strong hyperconjugation between π-electrons in the heterocyclic ring and on the substituent at the phosphorus atom. The most distinctive implication of this situation is a pronounced ionic polarization of the P—X bond, which prevails even in cases where electronegativity differences between P and X become small or negligible. This polarization serves as key factor to explain the extreme P—X bond lengthening and remarkable reactivities of many NHPs. Extensive studies have demonstrated the possibility to manipulate the bond polarization in a controlled way, offering access to species that span the whole range from molecules with predominantly covalent bonding to contact ion pairs with a close relation to frustrated Lewis pairs. It is hoped that this knowledge provides a sound basis to make NHPs potentially useful and versatile reagents in synthesis or catalysis.

Aside from the general aspects of P—X bond polarization, computational studies predicted that a reverse hyperconjugation in *P*-amino-NHPs allows for a moderate strengthening of the exocyclic at the expense of the endocyclic P—N bonds. The utilization of this effect in combination with ring anellation might offer an interesting route to generate phosphinidenes. Although the first NHPs with anellated ring systems have been described,[16] this hypothesis is still awaiting experimental proof, and the desire to do so provides a strong stimulation for the further exploration of the chemistry of NHPs.

BIOGRAPHICAL INFORMATION

Dietrich Gudat was born in Düsseldorf in 1957. He received his Diploma and doctoral degrees from the University of Bielefeld under the supervision of Prof. Edgar Niecke. After conducting postdoctoral research, including a period at Iowa State University with Prof. John G. Verkade, he went to the University of Bonn where he finished his Habilitation in 1995. Since 2002, he has been professor of Inorganic Chemistry at the University of Stuttgart, Germany. His research interests include the chemistry and application of compounds of main group elements and their complexes (with a strong focus on phosphorus compounds) and the application of multinuclear NMR spectroscopy in molecular inorganic chemistry.

FOOTNOTES

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