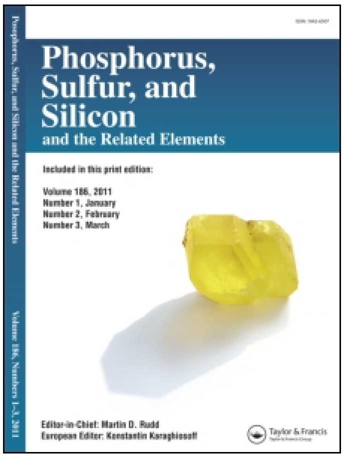

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Novel Aspects of Phosphorus Analogues of Arduengo Carbenes: from Very Stable Phosphenium Ions to Umpolung of P-H Bonds

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According to the results of structural and computational studies, *P*-halogeno-diazaphospholenes are not ionic but feature weak and polar covalent P-X bonds. Similar bond weakening effects which are attributable to l.p. (N)-σ^*(P-X) hyperconjugation were also established for *P*-H substituted diazaphospholenes. The physical properties of these compounds suggest a hydridic nature of the P-H bond, and their reactivities display an "Umpolung" as compared to known reaction patterns of phosphines.

Keywords: phosphorus heterocycles; structure correlation; bond ionicity; phosphines; Umpolung

INTRODUCTION

Imidazoylidenes (I) [1] represent one of the first examples for stable carbenes whose discovery incited not only intensive studies of the chemical properties of the carbenes themselves, but stimulated exploration of compounds featuring other main group elements in a similar bonding situation. Beside homologues of I with heavier group 14 elements, also isoelectronic phosphorus cations II were prepared in this context.[2]

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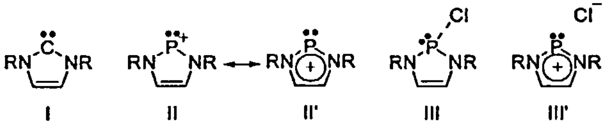
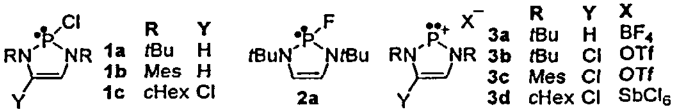


One common feature of the heterocycles **I, II** is the possibility of aromatic stabilization of the 6π-electrons in the ring. Extensive investigations revealed that for carbenes aromaticity is of little importance and the bonding is best represented by a mesomeric structure **I** with a localized CC double bond.[3] In contrast, for the phosphorus cations cyclic π-delocalization as expressed by resonance structure **II'** was postulated to have a strong stabilizing effect. In particular, the presence of a remarkably long P-Cl bond of 2.75 Å in **III** was attributed to a high degree of π-delocalization and lead the authors to formulate this compound as a salt **III'** with an aromatic phosphenium cation.[2][4]

The contrary assessment of the properties of the isoelectronic species **I, II** caught our attention, and we set out for a detailed investigation of the bonding in the phosphorus compounds **II, III.**[5] The results shown here demonstrate how (i) structure correlation involving a series of related molecules (scheme 1) together with computational studies can be used to obtain insight into the bonding situation and to explain the unique weakening of the P-Cl bonds, and (ii) that the derived concepts are of more general relevance and can be extended to achieve deliberate destabilization of P-H bonds which culminates in "Umpolung" of the chemical reactivity of *P*-Hydrido-diazaphospholenes as compared to known reaction patterns of phosphines.



	R	Y
1a	tBu	H
1b	Mes	H
1c	cHex	Cl

	R	Y	X
3a	tBu	H	BF_4
3b	tBu	Cl	OTf
3c	Mes	Cl	OTf
3d	cHex	Cl	$SbCl_6$

SCHEME 1: Molecular structures of studied P-halogeno-diazaphospholenes and diazaphospholenium salts.

STRUCTURE CORRELATION

The set of compounds used for structure correlation includes the *P*-

chloro and *P*-fluoro diazaphospholenes **1a-c**, **2a**, and the diazaphospholenium salts **3a-d** which were either prepared in analogy to published procedures or whose structural data were taken from the literature.[5] Relevant bond distances are listed in Tab. 1.

	P-X	P-N	N-C	C-C
1a	2.6915(4)	1.6628(8) 1.6651(8)	1.3912(12) 1.3913(12)	1.3485(14)
1b	2.3241(4)	1.6734(10) 1.6750(11)	1.4057(15) 1.4015(16)	1.3378(18)
1c[2a]	2.416(2)	1.587(3) 1.672(3)	1.390(6) 1.396(5)	1.320(6)
2a	1.6544(14)	1.672(2) 1.6721(19)	1.415(3) 1.415(3)	1.336(3)
3a		1.6579(14) 1.6654(14)	1.368(2) 1.370(2)	1.353(2)
3b	-	1.6662(15) 1.6708(15)	1.374(2) 1.378(2)	1.351(2)
3c	-	1.6580(16) 1.6713(16)	1.369(2) 1.378(2)	1.353(3)
3d[6]	-	1.656(4) 1.673(4)	1.363(6) 1.370(6)	1.351(7)

TABLE 1: Relevant bond lengths in diazaphospholene compounds

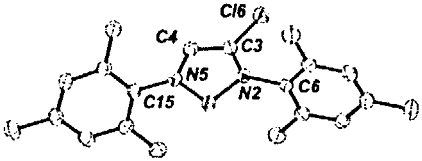


FIGURE 1: Molecular structure of the cation of crystalline **3c** without H-atoms.[5] Relevant distances (Å): N2-C3 1.378(3), N2-C6 1.464(4), N5-C4 1.370(3), N5-C15 1.460(4).

Comparative analysis of the data lead to the following conclusions:

(a) Genuine diazaphospholenium cations in triflate and BF_4 salts (**3a-d**) display planar rings with bond distances intermediate between single and double bonds. Considering that in the cation of **3c** (Fig. 1) the endocyclic C-N bonds are by ca. 10 pm shorter than the exocyclic ones (which constitute pure single bonds due to the orthogonality of the arene rings to the lone pairs at N), the bond length equalization can be taken as direct evidence for the presence of 6π-delocalization. Since the endocyclic bonds in all cations are indistinguishable, the extent of this effect is independent of the nature of the exocyclic substituents.

(b) Structural comparison between the *P*-fluoro compound **2a** and the cations of **3a-d** reveals only small changes following the formation of a strong covalent bond between the phosphorus and an exocyclic halogen atom: the rings are no more planar and display flat envelope conformations, but except from a slight lengthening of the N-C bonds, the endocyclic bond distances are hardly altered. In the view of these results, the small structural deviations between **1a** and the cations of **3** represent almost half of the difference between an ionic and a molecular species and can thus no longer be taken as proof for the ionic nature of **1a**.

(c) The P-Cl distances in **1a-c** exceed standard covalent bond lengths and vary further by some 40 pm depending on the substituents at the C and N atoms. At the same time, the endocyclic bonds show only minor changes which bear no correlation with the P-Cl bond lengthening.

In summary, these findings suggest that the P-X (X = Cl, F) interactions in all molecules are covalent bonds. The observed P-Cl bond lengthening owes to a bond weakening effect whose extent depends on the substituent pattern of an individual compound and is not entirely transmitted via the π-electron system. Computational studies [5] revealed that the bond weakening goes with an increase in ionic character of the P-X bonds and originates from two basic effects, (i) hyperconjugation interaction between the π-electrons in the C_2N_2 moiety and the empty σ*(P-X) orbital (Fig. 2; this interaction can be termed "σ*-aromaticity"), and (b) σ-bond polarization effects transmitted by the different electron releasing power (-I effect) of the substituents.

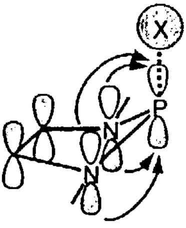


FIGURE 2: $\pi(C_2N_2)$-σ*(P-X) hyperconjugation in diazaphospholenes

UMPOLUNG OF P-H BONDS

The mechanisms which allow to tune the P-Cl bond ionicity in diazaphospholenes should as well be applicable to other phosphorus-element bonds. The case of P-H bonds was considered as particularly interesting for the following reason: phosphorus hydrides behave in chemical reactions as the source of a proton, however, since the similar electronegativities of both elements render these bonds rather unpolar, it can be conceived that electronic tuning by effects as the described hyperconjugation might enhance the hydridic character of the P-H moiety and permit "Umpolung" of the commonly observed reactivity pattern.

To test this hypothesis, we synthesized the P-hydrido-diazaphospholenes **4a-c** by $LiAlH_4$ or $LiBEt_3H$ reduction of **1a-c**.[7] An X-ray crystal structure analysis of **4c** revealed the presence of a distinctly folded five membered ring whose endocyclic bonds are still not completely localized, even though the remaining bond length equalization is still lower than in **1c**. The P-H distance (1.51(4) Å) is distinctly longer than the value of 1.29±1 Å commonly found in crystal structures of phosphines and indicates together with the observed red-shift of νP-H in the IR ($\nu \approx 2120 - 2202$ cm^{-1}) and remarkably low values of $^1J_{PH}$ (219 – 137 Hz) in the NMR spectra of **4a-c** significant bond weakening. This was corroborated by computational studies whose results revealed that the decrease in covalent bond order is paralleled as expected by an increased hydridic polarization of the P-H bond.

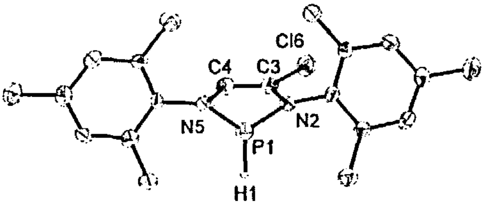
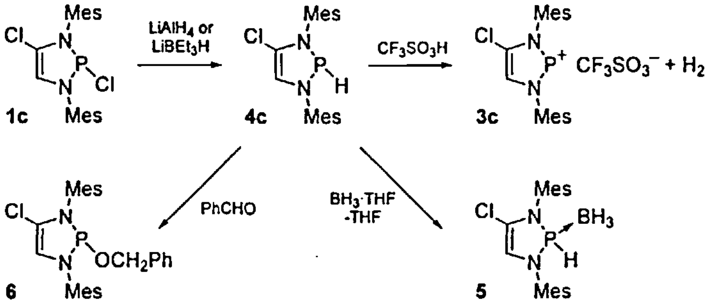


FIGURE 2: Molecular Structure of 4c.[6] with H-atoms other than H1 omitted. Relevant distances (Å): P1-H1 1.51(4), P1-N5 1.709(3), P1-N2 1.722(3), N2-C3 1.407(5), C3-C4 1.327(5), C4-N5 1.410(5).

Investigations of model reactions indicated that the hydridic polarization of the P-H bond derived from the spectroscopic studies is in fact accompanied by Umpolung of its chemical reactivity.[7] Thus, reaction of **4c** with CF_3SO_3H proceeded not as commonly observed for phosphines by protonation to afford a *phosphonium* salt, but rather by evolution of H_2 and formation of the *phosphenium* salt **3c**. Remarkably, the reaction occurred even at -78°C spontaneously and without NMR spectroscopically detectable intermediate. This unusual reactivity is not caused by insufficient basisicity of the phosphorus, since **4c** was shown to react readily with $BH_3 \cdot THF$ to form the stable adduct **5**. Finally, reaction of **4c** with benzaldehyde was found to proceed with inverse regioselectivity as normally observed for phosphines, yielding instead of an α-hydroxyphosphine the benzyloxy compound **6** whose constitution was unequivocally verified from a ^{13}C-DEPT NMR spectrum.



SCHEME 2: Synthesis and reactivity of a *P*-hydrido-diazaphospholene

References

[1] A.J. Arduengo, R.L. Harlow, M. Kline, *J. Am. Chem. Soc.* **113**, 361 (1991).

[2] (a) I.A. Litvinov, V.A. Naumov, T.V. Gryaznova, A.N. Pudovik, A.M. Kibardin, *Dokl. Akad. Nauk SSSR* **312**, 623 (1990); (b) M.K. Denk, S. Gupta, A.J. Lough, *Eur. J. Inorg. Chem.*, 41 (1999).

[3] D. Bourissou, O. Guerret, F.P. Gabbai, G. Bertrand, *Chem. Rev.* **100**, 39 (2000), and cited refs.

[4] (a) M.K. Denk, S. Gupta, R. Ramachandran, *Tetrahedron Lett.* **37**, 9025 (1996); (b) C.J. Carmalt, V. Lomeli, B.G. McBurnett, A.H. Cowley, *J. Chem. Soc. Chem. Commun.*, 2095 (1997).

[5] D. Gudat, A. Haghverdi, H. Hupfer, M. Nieger, *Chem. Eur. J.*, in press.

[6] A.M. Kibardin, I.A. Litvinov, V.A. Naumov, Yu. T. Struchkov, T.V. Gryaznova, Yu. B. Mikhailov, A.N. Pudovik, *Dokl.. Akad. Nauk SSSR* **298**, 369, (1988).

[7] D. Gudat, A. Haghverdi, M. Nieger, *Angew. Chem. Int. Ed. Engl.* in press.