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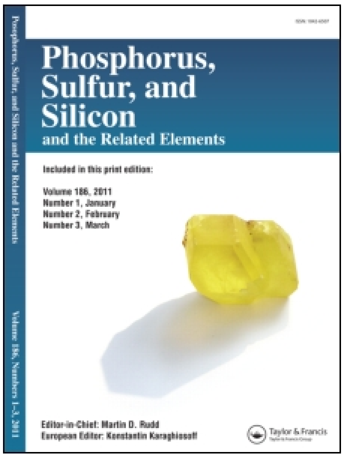

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HIGH STABILITY OF A PHOSPHENIUM ION ALLOWS UMPOLUNG OF P—H BONDS

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The high intrinsic stability of 1,3,2-diazaphospholenium cations enhances ionic polarization of covalent P—X bonds in P*-halogeno- and* P*-hydrido-diazaphospholenes. The physical properties of the latter suggest a hydridic nature of the P—H bond, and their reactivities display an "Umpolung" as compared to known reaction patterns of phosphines.*

Keywords: Bond dissociation; element hydrides; phosphines; phosphorus heterocycles; Umpolung

INTRODUCTION

Element-hydrogen (E—H) bonds belong to the most widely used functional groups in chemistry. Their reactivity follows a regular trend which is strongly correlated with bond polarities and implies a change from hydridic ($E^{\delta+}$—$H^{\delta-}$) to protonic ($E^{\delta-}$—$H^{\delta+}$) character of the hydrogen atom. P—H bonds in phosphanes R_2PH display, despite their low polarities (due to the similar electronegativities of both elements: $\chi^{AR} = 2.06$ (P), 2.20 (H)), a pronounced disposition for "protic" reactivity (cf. Scheme 1) which is attributable to the greater stability of most R_2P^- as compared to R_2P^+ fragments. In consideration of this aspect it appears conceivable to induce an "Umpolung" of the reactivity by optimizing the stability of the cation fragments. Taking into account the high intrinsic stability of heterocyclic 1,3,2-diazaphospholenium cations **1** (Scheme 2), *P*-substituted diazaphospholenes **2** are interesting target compounds for this purpose. Here, we give an account on our accomplishments concerning (1) the quantification of cation stabilities of the cations **1**, (2) evaluation of the bond polarization induced by a diazaphospholenium

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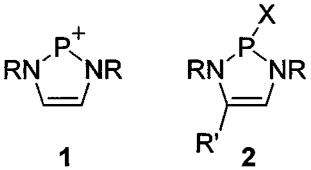
$$R_2PH \longrightarrow [R_2P]^+ + H^- \quad \text{(a)}$$

$$R_2PH \longrightarrow [R_2P]^- + H^+ \quad \text{(b)}$$

SCHEME 1 Hydridic (a) and protic (b) reactivity of a phosphane.



1 **2**

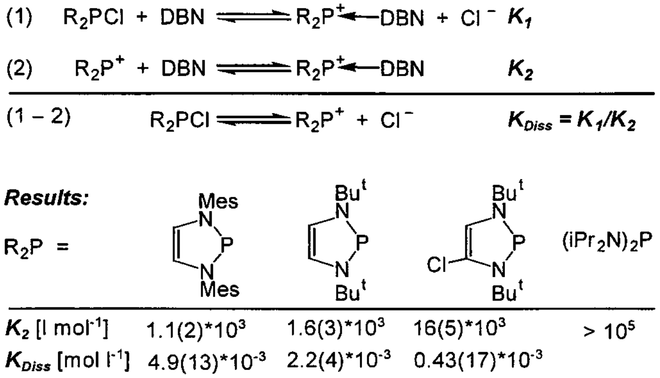
SCHEME 2 Studied diazaphospholene compounds.

fragment on adjacent P—X (X = F, Cl, H) bonds in compounds **2**, and (3) the exploitation of this effect to promote a hydridic reactivity of *P*-Hydrido-1,3,2-Diazaphospholenes.

CATION STABILITIES AND P—X BOND POLARIZATION IN DIAZAPHOSPHOLENE SYSTEMS

Considering that the stability of phosphenium cations is mirrored in their ability to form adducts with nucleophiles,[1] we studied Lewis-acid/base reactions of diazaphospholenium ions using both computational and experimental methods.

A theoretical estimation of relative cation stabilities was obtained from a computational study of hydride transfer reactions and revealed that the excess stabilization attributable to the CC double bond in the five-membered ring of cations **1** ($\approx$21 kcal mol^{-1} for $R = R' = H$) is similar to the effect induced by di-alkylation of an the diaminophosphenium ion $[(H_2N)_2P]^+$ ($\approx$14 kcal mol^{-1}).[1] An experimental approach to the comparison of cation stabilities involved the determination of equilibrium constants for the formation of Lewis-acid/base adducts between phosphenium ions and diazabicyclononene (DBN) from NMR titrations, and revealed cations **1** to be less electrophilic than open chain diaminophosphenium ions by one to two orders of magnitude (Scheme 3).[2] Extension of this approach to measurement of the corresponding association constants of *P*-chloro-diazaphospholenes **2** (X=Cl) allowed to compute P—Cl bond dissociation constants. The results suggest a unique weakening of the P—Cl bonds in **2** which was corroborated by further structural, spectroscopic, and conductometric studies. A computational analysis allowed to identify a combination of $\pi(C_2N_2) \rightarrow \sigma^*(P—Cl)$ hyperconjugation (Figure 1) and inductive effects by strongly electron releasing peripheral substitutents as the origin of the observed effects.[2]



SCHEME 3 Evaluation of P—Cl bond dissociation constants from Lewis acid/base association constants.

UMPOLUNG OF P—H BONDS

To test the hypothesis if hyperconjugative tuning can enhance the hydridic character of a P—H moiety, we synthesized the hydrides **3** (R = ^{t}Bu, Mes; R′ = H, Cl) from **2**.[3] Significant P—H bond weakening was indeed suggested by the observation of marked red-shifts of νP—H in the IR spectra ($\nu \approx$ 2120–2202 cm^{-1}) and a remarkably long P—H bond (1.51(4) Å) in an X-ray crystal structure of **3a** (R = Mes; R′ = Cl). Computational studies confirmed that these effects correlate with lower covalent bond orders and increased hydridic polarization of the P—H bond.

Studies of model reactions indicated that this bond polarization is in fact accompanied by Umpolung of its chemical reactivity. Thus, reaction of **3a** with CF_3SO_3H proceeded at −78°C by evolution of H_2 and

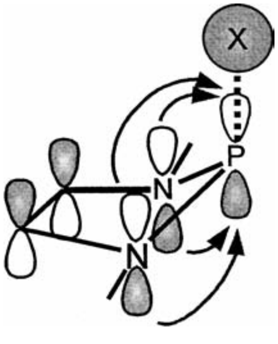
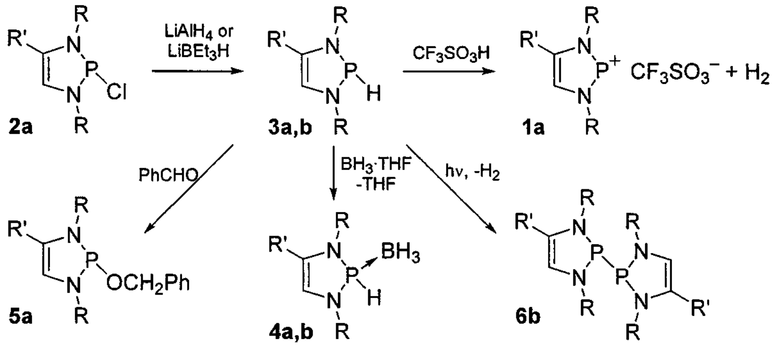
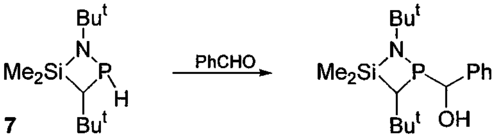


FIGURE 1 $\pi(C_2N_2) \rightarrow \sigma^*(PCl)$ hyperconjugation in 2-halogenodiazaphospholenes.

formation of a *phosphenium* salt **1a**.[3] The failure to observe a reaction involving *P*-protonation to a *phosphonium* salt is not attributable to low nucleophilicity at phosphorus, since **3a,b** form stable adducts with $BH_3 \cdot THF$.[4] Addition of **3a** to benzaldehyde proceeded with inverse regioselectivity as normally observed for phosphines, yielding instead of an α-hydroxyphosphine the benzyloxy compound **5**.[3] A unique result is the photochemically induced dehydrogenation of **3b** ($R = tBu$; $R' = H$) to give the sterically hindered diphosphane **6b**.[4]



The assumption that cation stability rather than conformational effects or steric strain is the driving force for the observed reactivity is supported by the failure to observe similar "Umpolung" effects for the four-membered cyclic phosphane **7** whose conjugated cation is much less stable as compared to **1**.[5]



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