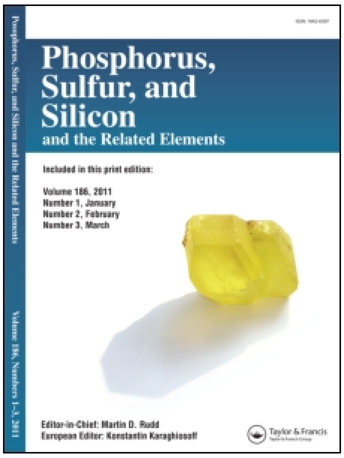

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Substituent Effects on Geometries of Iminophosphanes and Disphosphenes. The Effect of σ-Push-Pull Substitution

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SUBSTITUENT EFFECTS ON GEOMETRIES OF IMINOPHOSPHANES AND DISPHOSPHENES. THE EFFECT OF σ-PUSH-PULL SUBSTITUTION

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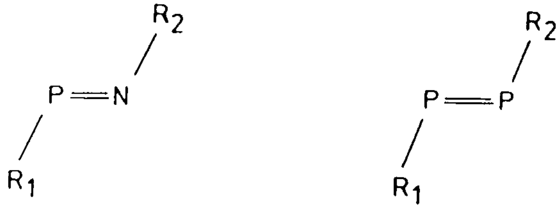
Abstract. The combination of electron withdrawing/donating substituents (*σ-push pull* substituents) causes unusual bonding features in iminophosphanes and diphosphenes, as explored by quantum chemical ab initio calculations at SCF and MCSCF level. For the diphosphenes the predictions are confirmed by a selected variety of double bond systems, synthesized and structurally characterized for this purpose.

The flowering of the chemistry of low coordinated P(III) double bonded system ist best witnessed in the richness of experimental structures hitherto reported on iminophosphanes[1,2].



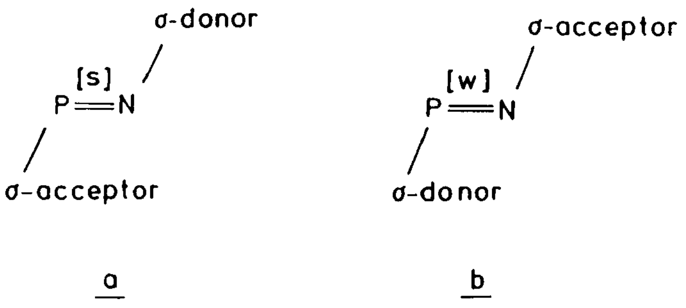
a

b

1

It prompted us to develop a general theory of substituents on the structures of iminophosphanes[3], 1a, and the electronically related substituted diphosphenes[4], 1b. In fact it will be shown that substituents can cause considerable deformation of geometry, different in 1a compared with 1b. *σ-push-pull* substitution, 2, results novel structural features in these systems.

In case of the **iminophosphanes**, <u>1a</u>, trans to cis isomerization occurs with a (relatively) low energy barrier for nitrogen inversion[5]. Quantum chemical calculations[3] indicate a strong dependence of the N-inversion barrier on the substituents R_1 and R_2; e.g., for trans to cis isomerization R_1/R_2=H/H 13.5 [kcal per mole], F/H 7.3; Cl/H 9.0; NH_2 (planar)/H 8.9, H/CH_3 12.9; H/SiH_3 2.0 [determined by location of ground state and transition state geometries]. Hence electronegative substituents at P and/or electropositive substituents at N extremely lower the N-inversion barrier. Concomitantly the lowering of the N-inversion barrier (e.g., R_1=F, R_2=SiH_3) pronounces ground state geometries with short PN double bonds and makes the nitrogen environment more linear. In more detail on the basis of the quantum chemical analysis[3] one can differentiate between two classes of *σ-push-pull* substitution. In <u>2a</u> the central PN bond will be strengthened (s) or as in <u>2b</u> weakened (w) due to substituent effects[3]. Theory is in full accord with experiment which results iminophosphanes with a short (PN=150.0 (pm), R_1=OMes*, R_2=Mes^{*6}) or a long (PN=159.8, R_1=TMP [tetramethylpiperidyl], R_2=N(SiMe$_3$)$_2$^{7}) central π-bond. For substituents capable of additional π-mesomeric interactions, R_1=R_2=NH_2, the σ-effects superimpose the π-effects. They can be additive or counteractive. Again it is in full accord with experiment[1,2].



<u>2</u>

[s] strengthen

[w] weaken

In case of **diphosphenes**, 1b, the combination of σ-electron withdrawing/donating substituents causes a different effect, the attempted briding in *push-pull* substituted diphosphenes, 3.

a

b

X = halogen

3

Quantum chemical calculations on a variety of model systems 3 (X=F, Cl, NH_2, CH_3, H) evidence a decrease of the valence angle ∢ HPP, even below 90 degrees, with increasing electronegativity of X. An analysis of the overall electron densities in these structures indicates strong charge separation between X and P(1). In other words the structure 3b is pronounced, a close ion pair of X^- with a P_2H^+, the latter with a nonclassical three-center bond[4]. The most stringent test to the model of attempted bridging in σ-*push-pull* substituted diphosphenes is 1b with R_1=TMP [tetramethylpiperidyl], R_2=P(N(i-propyl)$_2$) with ∢PPP=89.4 degrees[4].

Further quantum chemical investigations lead to the following general conclusions: (1) For 10 electron species HXY (X,Y=C,Si,N,P etc.) a linear geometry is prefered in case one of the constituents X(Y) is of the first long period (C,N) and the other from the higher long periods (Si,P) with the heavy atoms always terminal rather than central. For HXY with X and Y constituted both from higher rows, a bridged nonclassical structure is observed, as predicted previously for Si_2H_2[8].

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