Frontier Orbital Crossing and Ambident Reactivity in Phosphorus(III) Systems with (p–p) π-Bonds

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Phosphorus(III) double bonded systems possess two energetically closely spaced HOMOs, π and σ, and if the orbital sequence HOMO/LUMO is π/π*, a [2 + 2] cycloaddition route is followed, while with a σ/π* sequence [2 + 1] or [4 + 1] cycloadducts are formed; owing to σ and π orbital crossing, increasing the electronegativity of a π-donating ligand X favours the latter paths.

The synthesis of compounds containing (p–p) π-bonds at phosphorus(III) and studies on their reactivity are of current interest.[1,2] Phospha-alkenes (**1**; X = C<) as well as amino-iminophosphanes (**1**; R = N–, X = N–) dimerize to (**2a,b**), because weakly bonded π-systems tend to undergo [2 + 2] cycloaddition reactions. On the other hand, the alkyl substituted iminophosphane (**1**; R = Bu^t, X = N–Bu^t) forms[3] a three-membered ring system (**3**), *via* [2 + 1] cycloaddition, and the oxaphosphane (**1**; R = Bu^t, X = O) adds[4] to 1,3-diketones *via* a [4 + 1] cycloaddition. Hence the reactivity of (**1**) depends on the nature of X.

We now present theoretical evidence that (**1**) can react as a 1,2-dipole[5] *or* as a 1,1-dipole with the reactivity depending on the electronegativity of X. It will be shown that the ambident reactivity of (**1**) is due to an orbital crossing of two HOMOs.

Within the concept of frontier orbital theory[6] the route for a reaction depends on the nature of the frontier orbitals. For (**1**), energetically high lying orbitals are provided from the PX π-bond (π,π*) and the lone pair at the phosphorus atom (σ). *A priori*, two extreme bonding situations can be differentiated. (a) The HOMO is a π-orbital and the LUMO is the π*-orbital of the PX double bond. In this case, [2 + 2] cycloaddition will be preferred, yielding (**2a,b**). (b) Alternatively, the HOMO is a σ-orbital (lone pair at P) and the LUMO is the π*-orbital of the PX double bond. Hence, the sequence of frontier orbitals is the same as that in a carbene.[7] Compound (**1**) could undergo [2 + 1] cycloaddition with itself and lead to (**3**), or could be trapped by *cis*-conjugated dienes *via* a [4 + 1] cycloaddition. On this basis, (**1**) can be considered formally[5] as a 1,2-dipole or a 1,1-dipole.

In order to examine the ordering of the orbital levels in the parent systems (**1a—c**), we determined the equilibrium

(1)   (2a)   (2b)   (3)
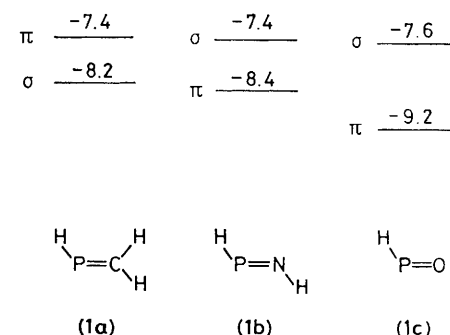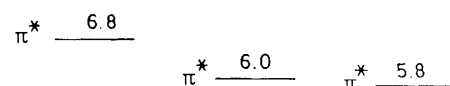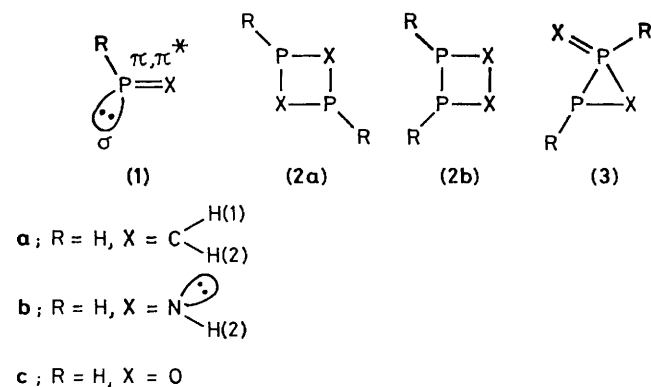
a ; R = H, X = C
b ; R = H, X = N
c ; R = H, X = O

Figure 1. Sequence of energies (in eV) of the orbitals σ and π, π* in (**1**), obtained from complete energy-optimized *ab initio* STO/3G calculations.

Table 1. Bonding parameters for (1a—c).

	Distances/Å				Angles/°		
	H–P	P–X	X–H(1)	X–H(2)	H–P–X	P–X–H(1)	P–X–H(2)
(1a)[a]	1.39	1.62	1.08	1.08	97.1	126.0	121.0
(1b)	1.40	1.58	—	1.05	96.1	108.9	—
(1c)	1.41	1.51	—	—	99.1	—	—

[a] Values are in close agreement with those determined by microwave spectroscopy (M. J. Hopkinson, H. W. Kroto, J. F. Nixon, and N. P. Simmons, *J. Chem. Soc., Chem. Commun.*, 1976, 513).

structures by complete energy optimization (in all degrees of freedom) at an *ab initio* STO/3G level.[8] The resulting sequence of frontier orbitals is plotted in Figure 1, and bonding parameters are in Table 1. For (1a), the orbitals σ and π are close in energy, with π as the HOMO. In contrast, in (1b) or (1c) the ordering of the MOs σ and π is reversed. This can be rationalized within the framework of Hückel theory:[6b] the σ-orbital is nonbonding, and a change in the electronegativity of X will only slightly influence its energy level, whereas the π and π^* MOs will be lowered markedly by a first-order perturbation of their energies.[6b]

π-Donating or π-accepting substituents attached to the PX-system can further alter the splitting of the σ and π levels in the parent HPX system; *e.g.* consider (1) with R = NH_2 or X = $CHNH_2$ (*trans*). Since the amino-group acts as a π-donor, the π-MO should be raised in energy. This qualitative consideration agrees with (computationally less expensive) energy-optimized MNDO[9] calculations.† It explains the formation of [2 + 2] cycloadducts[1,2] for these species.

The [2 + 2] dimerization is symmetry-forbidden and occurs in two stages. On this basis the regioselectivity [formation of head-to-tail dimers (2a) or head-to-head dimers (2b)] is determined by the primary step, the first bond being formed between the positions with the largest orbital coefficients in the HOMO and LUMO.‡ Similar considerations can be

† The energy differences $E\pi - E\sigma$ (in eV) are as follows: (1; R = NH_2, X = CH_2) 2.4; (1; R = NH_2, X = NH, *trans*) 0.4; (1; R = H, X = $CHNH_2$) 1.7; (1a) 0.6; (1b) —1.6; (1c) —2.9.

‡ Two extreme cases can be recognized: (a) head-to-tail dimerization (2a) for R = π-donor, X = alkyl. The largest coefficients in the HOMO (which resembles that of a non-bonding allyl system) will be at the peripheral atoms (C,N). In the LUMO polarization causes the largest coefficient to be at the least electronegative atom (P). On this basis, the first bond is formed between P and C; (b) head-to-head dimerization (2b) for R = alkyl, X = CH-(π-donor). The largest coefficients in the HOMO are now at the peripheral atoms P and N, which then yields primary bond formation between two P atoms.

applied to the analysis of the [2 + 1] addition process, which corresponds to the addition of a 1,1-dipole to a 1,2-dipole. In the former the valency of the phosphorus atom is increased by two [analogous to the 1,2-addition of carbenes (1,1-dipoles) to olefins (1,2-dipoles)].

Our theoretical findings show the novel properties of (p–p) π-bonds at phosphorus(III). The same class of compounds (1) possesses two closely spaced frontier orbitals of different symmetry, the levels of which depend on the electronegativity of X and on π-donating (π-accepting) substituents attached to the π-system. The products obtained in cycloadditions depend on these factors.

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