The Barrier to Pyramidal Inversion in Isopropylphenyltrimethoxysilylphosphine

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Summary The decrease in the barrier to pyramidal inversion at phosphorus which is observed when a trimethylsilyl ligand is replaced by a trimethoxysilyl ligand is ascribed to negative hyperconjugation.

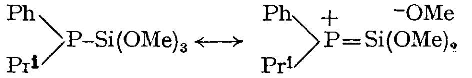
Recent findings have demonstrated that the magnitude of the barrier to pyramidal inversion in phosphines is influenced by many of the same structural effects which are well established in the analogous amines. Thus, the "normal" phosphorus inversion barrier of *ca.* 36 kcal mol^{-1} found for an acyclic trialkyl phosphine[1] may be lowered by the incorporation of substituents which (a) permit $(p-p)\pi$ conjugation[1,2] (b) are electropositive relative to alkyl groups[3] or (c) provide steric acceleration.[4] Although $(p-d)\pi$ conjugation has been invoked[5] to explain the enhanced inversion rates found[5] in diphosphines, we have shown[3] that these results may be satisfactorily interpreted on the basis of substituent electronegativity. We now report the first example of a system whose barrier height is clearly influenced by electronic factors other than simple ligand electronegativity or $(p-p)\pi$ delocalisation.

Table *Barriers to phosphorus inversion in* R^1R^2PX

Compound	R^1	R^2	X	$\Delta G^‡_T$ kcal mol^{-1} (T, °C)	Calculated[a] E_{inv} kcal mol^{-1}
(**1**)	Pr^i	C_6H_5	$Si(OMe)_3$	17·1 (57)	16·0
(**2**)	Pr^i	C_6H_5	$SiMe_3$	18·9 (62)[b]	18·4
(**3**)			$C(OMe)_3$		33·5[c]
(**4**)	Pr^n	c-C_6H_{11}	Me[d]	35·6 (130)	36·3

[a] These values were calculated for Me_2 PX using a specially parametrized CNDO/2 scheme; see A. Rauk, J. D. Andose, W. G. Frick R. Tang, and K. Mislow, *J. Amer. Chem. Soc.*, 1971, **93**, 6507. [b] See ref. 6. [c] The satisfactory agreement between the experimental and calculated values for (**1**), (**2**), and (**4**) provides a measure of credibility for the value calculated for (**3**). [d] The negligible difference in the phosphorus inversion barriers of methylphenyl-n-propylphosphine (32·1 kcal mol^{-1}) and methylphenyl-t-butylphosphine (32·7 kcal mol^{-1})[1] suggests that a change of X from Me to Bu^t will also have a negligible effect on the inversion barrier of (**4**).

As indicated in the Table, the inversion barrier of isopropylphenyltrimethoxysilylphosphine (**1**) is found to be *ca.* 2 kcal mol^{-1} *lower* than that of the analogous trimethylsilyl compound (**2**).[6] The trimethoxysilyl ligand may be regarded as considerably more electronegative than trimethylsilyl, and one might have anticipated, on this basis alone, a substantially *larger* barrier in (**1**) than in (**2**).† Evidently, the operation of an additional, presumably conjugative, interaction must here be considered, which compensates for the increased electronegativity of the trimethoxysilyl ligand. We submit that the observed effect is a manifestation of "negative hyperconjugation," a phenomenon which corresponds to a transfer of electron density from the phosphorus lone pair into antibonding orbitals of the trimethoxysilyl ligand. In valence-bond terms, this amounts to a contribution to the resonance hybrid from structures of the type depicted below. As with simple $(p-p)\pi$ conjugation, the extent of hyperconjugative delocalisation is expected to be maximal in the planar transition state for inversion.



It might be argued that the extent of delocalisation of the phosphorus lone-pair electrons into vacant *d* orbitals on the adjacent silicon atom is significantly enhanced in (**1**) relative to (**2**), because the electronegative methoxy ligands on silicon are expected to effect a contraction of the normally diffuse 3*d* orbitals,[7] and that the observed trend may thus be ascribed to $(3p-3d)\pi$ conjugation. However, it has been recognized[8] that hyperconjugation influences inversion barriers in systems composed entirely of first-row elements,‡ and the possibility that this effect may well be of comparable importance in systems containing second-row elements cannot be readily dismissed. Indeed, since the extraordinary barrier lowering accompanying the incorporation of a silicon atom adjacent to phosphorus (Table) may be explained quite readily without recourse to $(p-d)\pi$ conjugation,[3] there is no compelling reason to invoke this mechanism to interpret the barrier magnitude in (**1**). The calculated inversion barrier of (**3**) (Table) is of particular significance. Since there is no second-row element adjacent to the inversion centre in (**3**), $(p-d)\pi$ conjugation cannot be an important consideration, and the predicted barrier lowering of (**3**) relative to (**4**) is thus most plausibly ascribed to negative hyperconjugation. This phenomenon, therefore, also provides the most economic rationalisation for the observed barrier lowering of (**1**) relative to (**2**).

The planarity or near planarity at nitrogen in certain silylamines,[11] aminophosphines,[12] and sulphenamides[13] has been rationalised by invoking $(p-d)\pi$ conjugation, augmented by the presence of electronegative ligands on the acceptor atom. We propose that in many of these amines, the predominant structural influence upon pyramidal stability may well derive, as in the phosphines, from the effects of ligand electronegativity and hyper-conjugation.

Phosphine (**1**) was prepared by alkylation of sodium n-butyl phenylphosphinate[14] with isopropyl bromide, reduction with phenylsilane, and treatment of the resulting

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† A recent suggestion by D. Holtz (*Progr. Phys. Org. Chem.*, 1971, 8, 1) that electronegative ligands effect a decrease in pyramidal stability is contrary to the observation[3] that phosphorus inversion barriers exhibit a positive correlation with ligand electronegativity, with little differentiation among first- and second-row heteroatoms and among elements with and without lone electron pairs.

‡ For example, the nitrogen inversion barrier in isoxazolidines is lowered by several kcal mol^{-1} upon replacement of a methyl[9] ubstituent on nitrogen with a methoxymethyl[10] group.

isopropylphenylphosphine with sodium dispersion in refluxing dioxan followed by addition of trimethoxysilyl chloride.[15] The n.m.r. spectrum of (**1**) in [$^2H_8$]toluene at 0°, together with data for similar phosphines,[3,6] provides satisfactory evidence for the assigned structure. As the temperature is increased above 10 °C, the eight initially well-resolved signals in the isopropyl methyl region of (**1**) coalesce smoothly into four. The inversion barrier at coalescence, $\Delta G^{\ddagger}_{T}$ (Table), was determined by line-shape analysis as previously described[6] for (**2**). As expected for a first-order process, the barrier is concentration-independent.

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