Communications to the Editor

Effect of Ligand Electronegativity on the Inversion Barrier of Phosphines[1]

Sir:

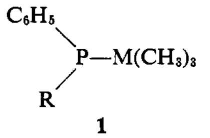
The major factors which govern the heights of pyramidal inversion barriers have been, as a matter of convenience, categorized as (a) strain effects, (b) electronegativity effects, (c) lone pair–lone pair repulsions, and (d) conjugative interactions.[2] However, no case is on record in which effects b and c have been convincingly disentangled. Furthermore, due to the possible existence of torsional barriers in many of the systems studied, the assignment of the observed exchange process to either rotation or inversion has introduced an ambiguity in interpretation whenever the heteroatom–heteroatom bond is not axially symmetric. We now wish to present what we believe to be the first clear-cut experimental evidence for the operation of an electronegativity effect on the magnitude of pyramidal inversion barriers.[3] Moreover, our findings eliminate the need to invoke (p–d)π conjugation as a significant factor in the barrier lowering.

Table I. Properties[a] of Phosphines $R(C_6H_5)PM(CH_3)_3$

Compd	$\Delta G^{\ddagger}_T$, °C kcal/mol	$M(CH_3)_3$, δ	$^3J_{PMCH}$, Hz	$CH_{3(a)}$, δ	$CH_{3(b)}$, δ	$\Delta\nu_{ab}$, Hz	$^3J_{HH(a)}$, Hz	$^3J_{HH(b)}$, Hz	$^3J_{PH(a)}$, Hz	$^3J_{PH(b)}$, Hz
1a[b]	32.7 (130)[c]	0.917	11.5							
1b	18.9 (62)	0.100	4.0	1.20	1.15	2.88	6.9	6.7	16.5	14.6
1c	21.4 (109)	0.192	3.3	1.16	1.11	3.12	6.9	6.7	16.4	14.7
1d[d]	19.3 (72)	0.129	1.7	1.10	1.07	1.74	6.9	6.7	16.4	15.0

[a] All compounds were purified by distillation at 50–70° (0.01–0.05 mm). Spectra were recorded on a Varian A-60A spectrometer. Except where noted, all values refer to *ca.* 30% v/v solutions in benzene-d_6 with *ca.* 5% v/v dioxane as internal standard. For **1b**, nmr data were obtained at *ca.* 30° and for the other compounds at *ca.* 40°. [b] Reference 5. [c] Racemization in decalin. [d] All values, except $\delta(M(CH_3)_3,)$ refer to solvent dioxane, since in benzene-d_6 the observed nonequivalence of the diastereotopic methyl groups is too small (*ca.* 0.5 Hz) for an accurate determination of the exchange rate at coalescence. Variable-temperature studies were performed in benzene-d_6, toluene-d_8, and dioxane at several concentrations, as well as upon a neat sample. In every case the estimated $\Delta G^{\ddagger}_T$ value occurred within the range 19.1–19.4 kcal/mol, although there was a considerable variation in the actual spectral parameters. Hence, the barrier is essentially solvent independent.

The series of phosphines, $R(C_6H_5)PM(CH_3)_3$ (**1a**–**d**), in which M represents an element of group IVa (C, Si, Ge, Sn), is ideally suited to probe the relative importance of effects b and c. The absence of nonbonded valence shell electron pairs on the substituent groups avoids complications due to electrostatic repulsion. The threefold axial symmetry of the $M(CH_3)_3$ group eliminates ambiguities resulting from torsional isomerism. Steric factors[4] as well as the slight rate enhancement which occurs through (p–p)π conjugation with the phenyl substituent[5] are expected to remain essentially constant throughout. Finally, in contrast to the nitrogen analogs,[7] the barrier to pyramidal inversion in **1b** is still easily measurable (18.9 kcal/mol),[8] even though it is approximately 16 kcal/mol lower than that in typical trialkylphosphines.[5]



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a, R = CH_3; M = C
b, R = $(CH_3)_2CH$; M = Si
c, R = $(CH_3)_2CH$; M = Ge
d, R = $(CH_3)_2CH$; M = Sn

Phosphines **1c** and **1d** were synthesized from isopropylphenylphosphine in a manner similar to that previously described[8] for **1b**. The nmr spectra provide convincing evidence foı the assigned structures. The relevant data are collected in Table I. Energy barriers at a temperature within the coalescence range,[8] $\Delta G^{\ddagger}_T$, were estimated using Binsch's[9] DNMR program for nmr line-shape analysis. Additional evidence that unimolecular pyramidal inversion at phosphorus is the rate process which corresponds to the measured barrier is provided by the invariance of the $^3J_{PMCH}$ coupling at temperatures well above coalescence, as well as by the insensitivity of the observed barriers for **1d** to variations in concentration.

As shown in Figure 1, the inversion barriers of **1a**–**d** (solid circles) correlate satisfactorily with the Allred[10] electronegativity values of the heteroatoms. Of particular interest is the observation that the barrier for **1c** is higher than that for *either* **1b** *or* **1d**. While the lower barrier of **1b** "might tentatively be ascribable to more effective (3p–3d)π as compared to (3p–4d)π

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[2] For recent reviews and leading references cited therein, see (a) A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem., Int. Ed. Engl.*, **9**, 400 (1970); (b) J. M. Lehn, *Fortschr. Chem. Forsch.*, **15**, 311 (1970).

[3] H. A. Bent, *Chem. Rev.*, **61**, 276 (1961).

[4] The absence of a steric effect due to the *tert*-butyl group in **1a** relative to other aryldialkylphosphines has already been demonstrated,[5] and steric effects in **1b**–**d** are expected to be even less significant.[6]

[5] R. D. Baechler and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 3090 (1970).

[6] For a discussion of nonbonded interactions in organometallic compounds of group IVa, see C. Frank Shaw, III, and A. L. Allred, *Organometal. Chem. Rev. A*, **5**, 95 (1970).

[7] For example, trisilylamine is planar, whereas trialkylamines normally have inversion barriers in the range 5–10 kcal/mol.[2]

[8] R. D. Baechler and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 4758 (1970).

[9] G. Binsch, *J. Amer. Chem. Soc.*, **91**, 1304 (1969).

[10] (a) A. L. Allred, *J. Inorg. Nucl. Chem.*, **17**, 215 (1961). This widely accepted[11] scale is a recent refinement of calculations based upon the Pauling thermochemical approach to atomic electronegativity. (b) See also A. L. Allred and E. G. Rochow, *ibid.*, **5**, 269 (1958).

[11] See, for example, F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry, A Comprehensive Text," Interscience, New York, N. Y., 1966, p 100.

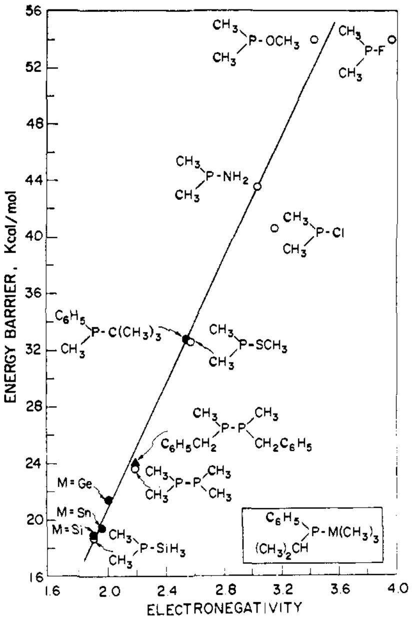

Figure 1. Energy barriers of pyramidal inversion *vs.* electronegativity.

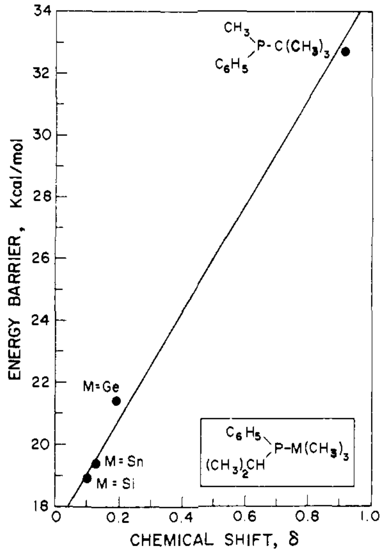

Figure 2. Energy barriers of pyramidal inversion *vs.* chemical shift of methyl protons (boldface) in benzene-d_6.

orbital overlap,"[8] the low barrier of **1d** is difficult to reconcile with this hypothesis. It is apparent that electronegativity *alone* accounts quite satisfactorily for these observations. Similarly the barrier to pyramidal inversion found[12] for 1,2-dibenzyl-1,2-dimethyldiphosphine, whose low value ($\Delta G^{\ddagger}_{155}$ 24 kcal/mol) had previously been ascribed to (3p-3d)π conjugation,[12] may now be accounted for entirely on the basis of the low electronegativity of the phosphorus ligand (triangle, Figure 1). Chemical shifts in closely analogous systems may be regarded as indicators of electron withdrawal.[13] It is therefore interesting to note the linear correlation (Figure 2) of proton chemical shifts for **1a-d** with barrier heights.

It is tempting to extrapolate our results to other cases in which delocalization of a lone electron pair on the inverting center into a vacant d orbital of an adjacent atom has been invoked to rationalize part or all of the observed lowering of inversion barriers; electronegativity of the adjacent atom may account for a substantial portion of the observed[15] effects.[16] Nevertheless, conjugative (including (p-d)π) effects may assume a significant role in certain systems with inversion centers other than phosphorus,[18] or in cases where the element adjacent to the inversion center bears electronegative substituents.

The data in Figure 1 may be enriched by calculated inversion barriers (open circles) for which experimental data are lacking.[19] Considering the large energy range covered (36 kcal/mol) and the circumstance that lone-pair repulsions and conformational heterogeneity might be expected to present complications, the additional data points fall into surprisingly close proximity to the line through the experimental points at the lower end of the electronegativity scale.[21] Apparently, for phosphines and perhaps for other inverting centers as well, inductive effects are indeed "sufficient to account for a large portion of the observed effect of heteroatomic substituents"[2a] on pyramidal inversion barriers, as suggested by independent nonempirical calculations.[23]

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(12) J. B. Lambert, G. F. Jackson, III, and D. C. Mueller, *J. Amer. Chem. Soc.*, **92**, 3093 (1970).

(13) It has been postulated[10b] that the proton chemical shifts in the $(CH_3)_4M$ system are a linear function of the electronegativity of M. However, the existence of this simple correlation has been questioned.[14]

(14) R. S. Drago and N. A. Matwiyoff, *J. Organometal. Chem.*, 3, 62 (1965).

(15) (a) (2p-3d)π: in silylamines; for relevant references concerning ground-state planarity at nitrogen see C. Glidewell, D. W. H. Rankin, A. G. Robiette, and G. M. Sheldrick, *J. Mol. Struct.*, **6**, 231 (1970); (b) (3p-3d)π: J. B. Lambert and D. C. Mueller, *J. Amer. Chem. Soc.*, **88**, 3669 (1966); J. B. Lambert, G. F. Jackson, III, and D. C. Mueller, *ibid.*, **90**, 6401 (1968); (c) (4p-4d)π: J. B. Lambert and G. F. Jackson, III, *ibid.*, **90**, 1350 (1968).

(16) This statement merely questions the importance of (p-d)π conjugation as a dominant influence upon the *difference* in energies of planar and pyramidal conformations, within the framework of the useful (though physically irrelevant in the MO scheme) *ad hoc* valence bond description of electronic structure.[2a] It is emphatically not intended as a commentary on the importance of such conjugation in *both* forms. This conclusion is in harmony with LCAO-MO-SCF calculations[17] on H_2NSiH_3, whose barrier height is essentially unaffected by the introduction of d orbitals on silicon, and with the very rough trend correlating nitrogen inversion barrier heights with electronegativity.[2b]

(17) J. M. Lehn and B. Munsch, *Chem. Commun.*, 994 (1970).

(18) T. G. Traylor, *Chem. Ind. (London)*, 649 (1963); F. A. L. Anet, R. D. Trepka, and D. J. Cram, *J. Amer. Chem. Soc.*, **89**, 357 (1967); J. M. Lehn and J. Wagner, *Chem. Commun.*, 1298 (1968); P. Koch and A. Fava, *J. Amer. Chem. Soc.*, **90**, 3867 (1968), whose scheme of "an internal displacement at sulfenyl sulfur" is, in fact, the orbital equivalent of pyramidal inversion at sulfinyl sulfur.

(19) These values were obtained using a specially parametrized CNDO/2 scheme which has been shown to give reasonable values of inversion barriers for a wide variety of systems containing first- and second-row elements.[20]

(20) A. Rauk, J. D. Andose, W. G. Frick, R. Tang, and K. Mislow, unpublished work.

(21) Hydrogen does not appear to fit this correlation, to judge by the value of its electronegativity (2.20)[10a] and that of the inversion barrier (37 kcal/mol) calculated[22] for phosphine by an *ab initio* scheme.

(22) J. M. Lehn and B. Munsch, *Chem. Commun.*, 1327 (1969).

(23) A. Rauk, L. C. Allen, and K. Mislow, unpublished work, cited in ref 2a.

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