Anal. Calcd. for $C_{32}H_{16}N_8GeCl_2$: C, 58.59; H, 2.46; Ge, 11.07; Cl, 10.81. Found: C, 58.70; H, 2.67; Ge, 11.1; Cl, 10.65.

Dihydroxygermanium Phthalocyanine.—Hydrolysis of the dichloride was slow with water, refluxing concentrated ammonia, live steam and refluxing pyridine. However, a 300 mg. sample of the sublimed dichloride was hydrolyzed completely with 20 ml. of refluxing 1:1 pyridine-concentrated ammonia solution in 6 hr. The blue hydroxide was not hygroscopic and dried completely at 110°.

Anal. Calcd. for $C_{32}H_{18}N_8GeO_2$: C, 62.17; H, 2.94; N, 18.13. Found: C, 62.88; H, 2.96; N, 17.74.

Treatment of the dichloride with concentrated sulfuric acid gave, after dilution and washing, dihydroxygermanium phthalocyanine, which was apparently uncontaminated with metal free phthalocyanine.

Diphenoxygermanium Phthalocyanine.—Reaction of 1.0 g. (0.0016 mole) of dihydroxygermanium phthalocyanine and 1.5 g. (0.016 mole) of phenol in 50 ml. of refluxing benzene for 3 hr. produced crystalline diphenoxygermanium phthalocyanine in very high yield. A 400 mg. sample of this product was heated at 385° for 2.5 hr. under a pressure of 2 microns in a sublimator equipped with an air cooled cold finger. A band of 17 mg. of uniform air stable crystals which were blue-green by transmitted light and reddish by reflected light was obtained.

Anal. Calcd. for $C_{44}H_{26}N_8GeO_2$: C, 68.51; H, 3.40; N, 14.53; Ge, 9.41. Found: C, 68.37; H, 3.46; N, 14.63; Ge, 9.18.

Bis-(*p*-phenylphenoxy)-germanium Phthalocyanine.—A mixture of 2.8 g. (0.016 mole) of *p*-phenylphenol and 1.0 g. (0.0016 mole) of the dihydroxide in 50 ml. of refluxing benzene gave a high yield of crystalline bis-(*p*-phenylphenoxy)-germanium phthalocyanine after 3 hr. A 300 mg. sample heated at 355° for 3.5 hr. at a vacuum of 2 microns yielded a ring of 17 mg. of uniform air stable crystals blue-green by transmitted and reddish by reflected light.

Anal. Calcd. for $C_{56}H_{34}N_8GeO_2$: C, 72.83; H, 3.71; N, 12.13. Found: C, 72.93; H, 3.96; N, 11.77.

Bis-(triphenylsiloxy)-germanium Phthalocyanine.—A mixture of 4.5 g. (0.016 mole) of triphenylsilanol and 1.0 g. (0.0016 mole) of the dihydroxide reacted in refluxing benzene in 3 hr. to give an almost quantitative yield of bis-(triphenylsiloxy)-germanium phthalocyanine. A 500 mg. sample of it heated at 390° for 2 hr. at a pressure of 2 microns gave 20 mg. of homogeneous air stable crystals which were blue-green by transmitted and reddish by reflected light.

Anal. Calcd. for $C_{68}H_{46}N_8GeSi_2O_2$: C, 72.16; H, 4.08; N, 9.87. Found: C, 71.52; H, 4.08; N, 9.71.

Discussion

In dichlorogermanium phthalocyanine the germanium is surrounded by two chlorine and four nitrogen atoms in what may be assumed to be octahedral fashion. This somewhat unusual hexacoordination and the size of the organic residue correlate well with the relative difficulty of hydrolysis of the dichloride (live steam gives complete hydrolysis only after 14 hr).

The replacement of the two chlorine atoms of dichlorogermanium phthalocyanine with simple or complex groups (H, C_6H_5 etc.) attached to the germanium by oxygen bridges is significant because these groups represent a type of metal phthalocyanine functionality not often fully used and because they deomonstrate the varied and complex nature of the residues which can be metal-bonded to phthalocyanines by this functionality.

The infrared spectrum of each of the compounds is characteristic and cannot in any case be ascribed to a mere mixture of reactants. Absorptions very near 700 cm.$^{-1}$ are found in the spectra of the phenoxy (700 cm.$^{-1}$), *p*-phenylphenoxy (705 cm.$^{-1}$) and siloxy compounds (702 cm.$^{-1}$). These absorptions may be attributed to the monosubstituted benzenes. The nearest absorption for the dichloride is at 690 cm.$^{-1}$ while the dihydroxide has none in the immediate neighborhood. Since all of the compounds show absorptions at 770–730 cm.$^{-1}$, this region cannot be used to further confirm the presence of monosubstituted benzene rings. Only two of the compounds have peaks in the 1270–1230 cm.$^{-1}$ area (1260 cm.$^{-1}$ for the phenoxy and 1250 cm.$^{-1}$ for the *p*-phenylphenoxy derivative). Possibly these absorptions may be due to the CO link.[4] The dihydroxide, dichloride, *p*-phenyl phenoxide and siloxide all show some absorption in the aromatic CH stretching region; however, in keeping with the low percentage of hydrogen this absorption is not particularly strong. The dihydroxide shows a strong peak at 3500 cm.$^{-1}$ which is undoubtedly due to OH stretching. When the dihydroxide is heated it does not volatilize, but it does change color slightly. In the spectrum of this new material the 3500 cm.$^{-1}$ peak is absent suggesting the formation of an oxygen bridged polymer $(C_{32}H_{16}N_8GeO)_x$.

Acknowledgment.—The authors are indebted to James Owen for collaborating in the development of some of the experimental methods.

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[4] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 114.

[CONTRIBUTION FROM THE CHEMICAL RESEARCH DEPARTMENT, CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID COMPANY, STAMFORD, CONNECTICUT]

The Basicity of Phosphines

BY WM. A. HENDERSON, JR., AND C. A. STREULI

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Equations have been derived which allow the prediction of the base strength of phosphines. The basicity of phosphines has been correlated with inductive, resonance, steric and hybridization effects. Important differences between the basicities of amines and phosphines are pointed out.

There is in the literature no comprehensive correlation of the structure of phosphines and their basicity toward a proton. Davies and Addis[1] determined the pK_a's of six methyl-substituted phenyldiethylphosphines in 50% ethanol and came to the conclusion that the steric effect of ortho-substituents is of lesser importance than the inductive effect. Brown[2] commented on the qualitative basicity series $Me_3P > Me_2PH > MePH_2 > PH_3$ and concluded that unlike the case for

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[1] W. C. Davies and H. W. Addis, *J. Chem. Soc.*, 1622 (1937).

[2] H. C. Brown, THIS JOURNAL, **67**, 503 (1945).

TABLE I

Compound	$\Sigma\sigma^{*}$[a]	pK_a[b]	Compound	$\Sigma\sigma^{*}$[a]	pK_a[b]
Tertiary phosphines			Secondary phosphines		
$(cyclo\text{-}C_6H_{11})_3P$	−0.450	9.70	$(cyclo\text{-}C_6H_{11})_2PH$	+0.190	4.55
$(CH_3)_3P$	.000	8.65	$(n\text{-}C_4H_9)_2PH$	+ .230	4.51
$C_2H_5P(CH_3)_2$	− .100	8.62	$(n\text{-}C_8H_{17})_2PH$	+ .230[c]	4.41
$(C_2H_5)_2PCH_3$	− .200	8.62	$(i\text{-}C_4H_9)_2PH$	+ .240	4.11
$(C_2H_5)_3P$	− .300	8.69	$(CH_3)_2PH$	+ .490	3.91
$(n\text{-}C_3H_7)_3P$	− .345	8.64	$(C_6H_5)_2PH$	+1.690	0.03
$(n\text{-}C_4H_9)_3P$	− .390	8.43	$(CNCH_2CH_2)_2PH$	+2.090[d]	0.41
$(n\text{-}C_5H_{11})_3P$	− .390[c]	8.33			
$(i\text{-}C_4H_9)_3P$	− .375	7.97	Primary phosphines		
$(CH_3)_2PCH_2CH_2CN$	+ .800[d]	6.35	$n\text{-}C_8H_{17}PH_2$	+0.850[c]	0.43
$C_6H_5P(CH_3)_2$	+ .600	6.49	$i\text{-}C_4H_9PH_2$	+0.855	−0.02
$(n\text{-}C_4H_9)_2PCH_2CH_2CN$	+ .540[d]	6.40			
$(n\text{-}C_8H_{17})_2PCH_2CH_2CN$	+ .540[c,d]	6.27	Phosphine	+1.470	−14[f]
$C_6H_5P(C_2H_5)_2$	+ .400	6.25			
$CH_3P(CH_2CH_2CN)_2$	+1.600[d]	3.61			
$(C_6H_5)_3P$	+1.800	2.73			
$(CNCH_2CH_2)_3P$	+2.400[d]	1.36			

[a] From ref. 9, p. 619. [b] While the absolute values of pK_a are not accurate to the second decimal place, the relative values reported here are good to ±0.02 pK units. [c] Value of σ^* taken as same as from $n\text{-}C_4H_9\text{-}$. [d] The σ^* value of Stevenson and Williamson.[5] [e] From thesis of Sujishi.[6] [f] Value of pK_a from kinetics data of Weston and Bigeleisen.[7]

the methylamines, the phosphines showed no evidence of B-strain. The basicity of phosphines toward other Lewis Acids has been investigated by several workers, and there are several review articles in the literature.[3]

We wish to report here a correlation of basicity and structure for a variety of primary, secondary and tertiary alkyl and aryl phosphines. Relative values of the basicity of phosphines, taken with but two exceptions from the work of one of the authors,[4] are given to 0.01 pK units in Table I. While the absolute values of pK_a are not this accurate, the theoretically significant relative values are. The pK_a values were determined by potentiometric titration in nitromethane. The experimental method and validity of the technique have been described elsewhere.[4]

In view of the signal success of Hall[8] in utilizing the Taft equation,[9] $\log k/k_0 = \sigma^* \rho^*$, to correlate the base strength of amines, we have utilized the same approach here. The pK_a values of the phosphines listed in Table I plotted *versus* the sum of the σ^* values for the substituent groups are shown in Fig. 1. It may be seen that the phosphines are grouped in three classes; primary, secondary and tertiary. Phosphine itself, with an estimated pK_a of −14, constitutes a fourth class.

The sixteen tertiary phosphine pK_a's were used to calculate by the method of least squares the line shown in Fig. 1. Similarly, a line for secondary phosphines was obtained. For the primary phosphines, a tentative (dashed) line was drawn using for the slope the average of the slopes for the tertiary and secondary phosphines. This approximation is permissable in view of the nearly identical slopes for amines and for tertiary and secondary phosphines.

It is interesting to note that the first two slopes are essentially the same and that the distance between lines is approximately constant. This does not hold for the change in pK_a in going to phosphine itself.

The equations for the three lines thus obtained and for the three lines obtained by Hall[8] for amines are given in Table II.

TABLE II

EQUATIONS CORRELATING pK_a AND $\Sigma\sigma^*$

Compound		
Phosphine		
Tertiary	$pK_a = 7.85 - 2.67\ \Sigma\sigma^*$	(1)
Secondary	$pK_a = 5.13 - 2.61\ \Sigma\sigma^*$	(2)
Primary	$pK_a = 2.46 - 2.64\ \Sigma\sigma^*$	(3)
Amine		
Tertiary	$pK_a = 9.61 - 3.30\ \Sigma\sigma^*$	(4)
Secondary	$pK_a = 12.13 - 3.23\ \Sigma\sigma^*$	(5)
Primary	$pK_a = 13.23 - 3.14\ \Sigma\sigma^*$	(6)

It can be seen from an inspection of Fig. 2 or of the slopes of equations 1–6 that phosphines are slightly less susceptible to inductive effects than are amines. Inspection of the intercepts of equations 1–6, or the values of pK_a for $\Sigma\sigma^* = 0$, shows that as a first approximation, a phosphine with a given number of alkyl substituents is a weaker base than an amine of the same $\Sigma\sigma^*$ value. It may be pointed out that the basicity series (N>P) obtains with other Lewis acids ($AlMe_3$, $GaMe_3$, BMe_3, BF_3) with the exception of BH_3 (P>N) [3b]

Visual inspection of Fig. 1 shows that there is a large variation in the base strength of primary,

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(3) (a) F. G. A. Stone, *Chem. Revs.*, **58**, 101 (1958); (b) W. A. G. Graham and F. G. A. Stone, *J. Inorganic Nuclear Chem.*, **3**, 164 (1956); (c) S. Ahrland, J. Chatt and N. R. Davies, *Quart. Rev.*, 265 (1958).

(4) C. A. Streuli, *Anal. Chem.*, **32**, 985 (1960).

(5) G. W. Stevenson and D. Williamson, THIS JOURNAL, **80**, 5943 (1958).

(6) S. Sujishi, Thesis, Purdue University, June, 1949.

(7) R. E. Weston and J. Bigeleisen, THIS JOURNAL, **76**, 3074 (1954).

(8) H. K. Hall, Jr., *ibid.*, **79**, 5441 (1957).

(9) In this equation, k and k_0 are rate or equilibrium constants for the substituted and reference compounds; σ^* is a constant reflecting the inductive effect of the substituent and ρ^* is the reaction constant. The properties and application of this equation has been reviewed by R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, ed., John Wiley and Sons, Inc., New York, N. Y., 1956.

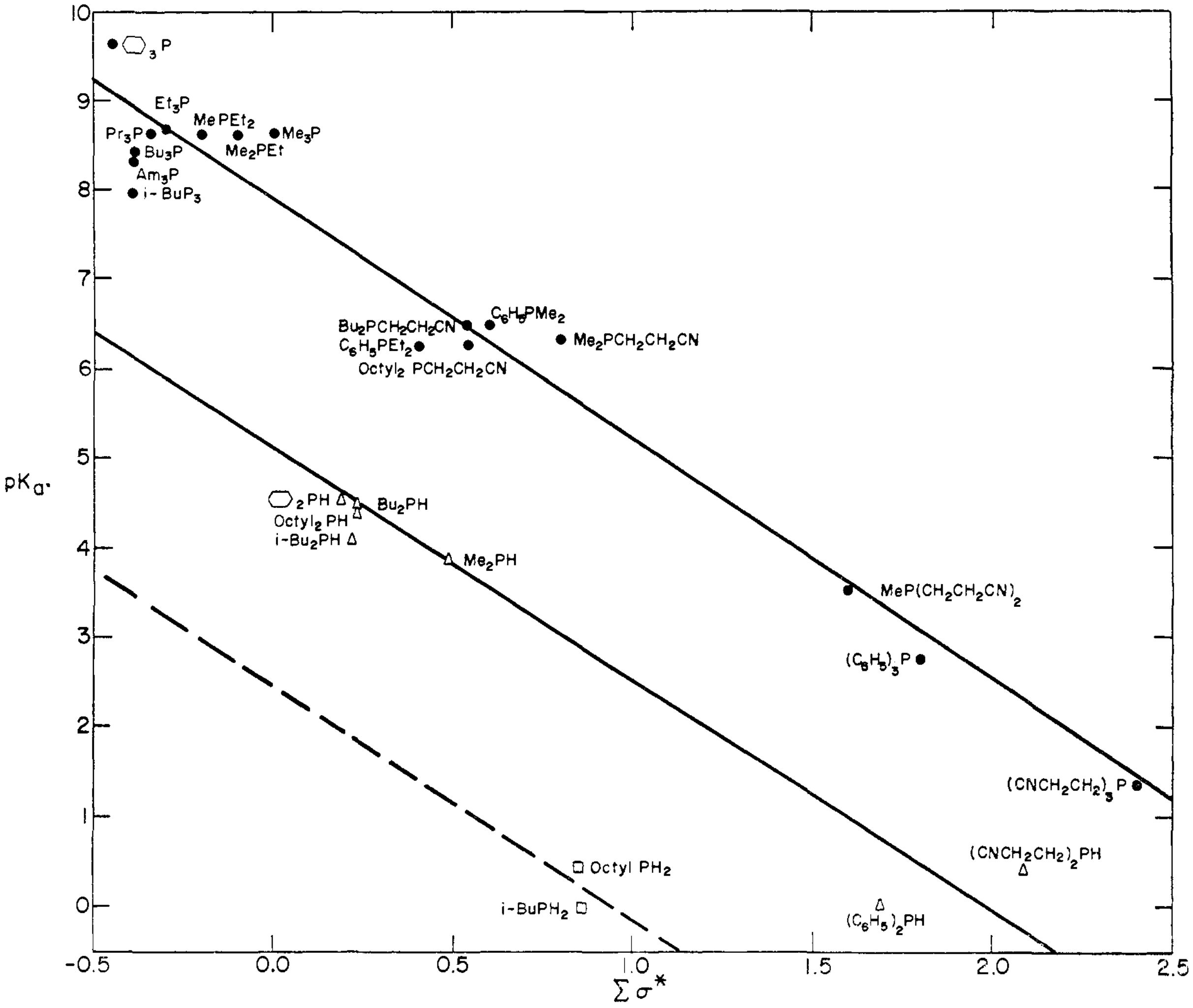

Fig. 1.—Plot of pK_a in water *versus* $\Sigma\sigma^*$ for phosphines.

secondary and tertiary phosphines, although the three series are to some extent overlapping. It is believed that an argument first proposed by Gibbs[10] and based on hybridization changes best explains the data. He suggested that the energy for reaction of the acid and base be divided into two parts, the energy needed for the base to assume sp^3 hybridization and the energy of formation of the new bond. From bond angle measurements it may be concluded that in going from phosphine itself to tertiary phosphines, there is a change from essentially p to sp^3 hybridization. Hence, the rehybridization energy would decrease markedly with increasing substitution.

In Hall's work on the different classes of amines, however, there is a smaller difference in the intercepts of the equations in Table II, and it is in the opposite direction, basicity varying in the order primary > secondary > tertiary. Here, hybridization is of little importance, as shown by the fact that there is little or no change in bond angle on going from ammonia to tertiary amines. The reverse order obtained is best explained by the solvation theory first suggested by Trotman-Dickenson[11] and later modified by Hall,[8] in which it is proposed that increasing the number of alkyl groups attached to nitrogen decreases the amount of solvation of N^+–H bonds in the product. The ammonium ion is thus of higher energy and thermodynamically less favored.

Inspection of Fig. 1 with special reference to the tertiary phosphines shows that within a given series the basicity of phosphines is largely determined by the inductive effect as measured by $\Sigma\sigma^*$. Other factors are also operative, but the basicity of a given tertiary phosphine is predictable within a pK unit provided that the σ^* values for the substituents are known.

Closer inspection of Fig. 1 reveals the fact that deviations from the pK_a predicted on the basis of inductive effect ($\Sigma\sigma^*$) are the result of steric effects. This is most clearly shown in the long series of trialkyl phosphines from trimethyl- to triisobutyl- where all the phosphines fall vertically off an hypothetical line of minimum steric hindrance[12] in the order of the bulkiness of the substituent groups. The consistency of the steric effect and hence its reality is shown by other points in the tertiary phos-

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[10] J. H. Gibbs, *J. Chem. Phys.*, **22**, 1460 (1954).

[11] A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1293 (1949).

[12] For an example of the use of this concept see R. W. Taft, Jr., THIS JOURNAL, **75**, 4231 (1953).

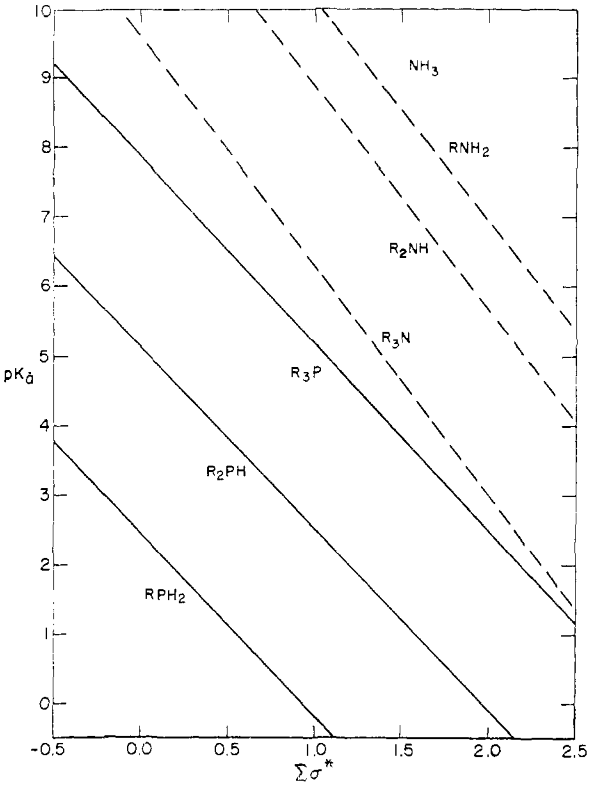

Fig. 2.—Plot of pK_a *versus* $\Sigma\sigma^*$ for phosphines and amines.

phine series and also by the points for secondary and primary phosphines.

The persistence of steric effects in the secondary and primary phosphines suggest the mode of operation of this effect. Since B-strain cannot occur in these phosphines, Brown's conclusion that B-strain is of no importance in the phosphines[2] must be accepted here also. Steric hindrance to attack by a solvated proton is unlikely, especially for secondary and primary phosphines, in view of the large size of the phosphorus atom and carbon–phosphorus bond. The existence of a steric effect is, therefore, ascribed to the varying amount of hindrance to solvation of the product phosphonium ion. Unlike the case for amines, where the solvation effect is important only in the primary and secondary series and invariant or negligible in the tertiary series,[4] the effect is still operative in the tertiary phosphines.

Figure 1 shows that the phenyl phosphines fall below the line by small but persistent amounts of the order of $^1/_2$ *pK* unit. While this may reflect a greater steric requirement of phenyl- than alkyl- or cyanoethyl-, it may also be a result of π-bond formation between the phosphorus atom and the benzene ring. The resulting electron delocalization would effect a lowering of the basicity of phenyl phosphines. The similar lowering of basicity of phosphines toward trimethylboron by vinyl groups was ascribed by Kaesz and Stone to operation of the same effect.[13]

The situation is quite different in the case of amines. The basicities of aniline, three N-alkylanilines and two N,N-dialkylanilines are lower than the values predicted by Hall's equations for alkylamines (Table II) by 2.4–4.0 *pK* units. This much larger decrease in basicity demonstrates the considerably greater importance of π-bonding in amines than phosphines and is part of the more general problem of weak double bond formation by the third row elements with carbon. While in the case of phosphorus, the lesser amount of double bond formation may to a first approximation be ascribed to a decrease in π-bond overlap occasioned by the greater length of the carbon-to-phosphorus σ-bond, final solution of the problem awaits exact calculation of the overlap integrals involved.

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[13] H. D. Kaesz and F. G. A. Stone, Abstracts of Papers, 135th Meeting, American Chemical Society, April 5, 1959.

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The Nucleophilicity of Phosphines

By Wm. A. Henderson, Jr., and Sheldon A. Buckler

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The nucleophilicity of phosphines has been investigated by following the kinetics of the reaction of phosphines with alkyl halides. The effect of substituents on the nucleophilicity of the phosphine is interpreted in terms of inductive, steric and bond hybridization effects. The effect of varying the alky halide, solvent and temperatures are reported. An anomalous reactivity has been found for methyl phosphines.

Within the last few decades, there has been published a huge volume of synthetic work dealing with phosphines and other trivalent phosphorus compounds, and incident to this work have appeared many speculations as to the mechanisms of the reactions involved. There have been, however, no definitive publications concerning the effect of structure on the reactivity of the free electron pair of those compounds, a knowledge of which is vitally necessary to intelligent discussion of mechanism. To the authors' knowledge there are no more than three relevant papers of limited scope in the literature, only one of which is quantitative in nature.[1] None of these treats nucleophilicity from a theoretical point of view.

Therefore, we have conducted a broad investigation of the nucleophilicity of phosphines as reflected by the rate of S_N2 attack on alkyl halides

$$R_1R_2R_3P + R_4X \longrightarrow R_1R_2R_3R_4P^{\oplus} + X^{\ominus} \quad (1)$$

The effects of varying the phosphine, the alkyl

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[1] W. C. Davies and W. P. G. Lewis, *J. Chem. Soc.*, 1599 (1934).