The basicity of phosphines

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The basicities of the triarylphosphines $P(4\text{-}XC_6H_4)_3$ (X = Cl, F, H, CH_3, CH_3O, $(CH_3)_2N$), $P(3\text{-}CH_3C_6H_4)_3$, and $P(2\text{-}CH_3C_6H_7)_3$ as well as the trialkylphosphines $P(t\text{-}Bu)_3$ and PCy_3 have been measured by the nitromethane titration method. The range of basicity available by aryl substitution is very large, being $pK_a = 8.65$ for X = $(CH_3)_2N$ to 1.03 for X = Cl. The most basic phosphine is $P(t\text{-}Bu)_3$ whose $pK_a = 11.40$. The measured basicities correlate well with σ_p, σ^ϕ, and ν as well as with the lone pair ionisation potentials of the triarylphosphines. Generally the ^1H, ^{31}P, and ^{13}C nmr spectral parameters of the free and protonated phosphines do not correlate well with pK_a.

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Utilisant la méthode de titration au nitrométhane, on a mesuré les basicités de triarylphosphines $P(4\text{-}XC_6H_4)_3$ (X = Cl, F, H, CH_3, CH_3O, $(CH_3)_2N$), $P(3\text{-}CH_3C_6H_4)_3$ et $P(2\text{-}CH_3C_6H_7)$ et des trialkylphosphines $P(tert\text{-}Bu)_3$ et PCy_3. L'éventail des basicités disponibles pour la substitution des groupes aryles varie de $pK_a = 8{,}65$ pour X = $(CH_3)_2N$ à 1,03 pour X = Cl. La phosphine la plus basique est la $P(tert\text{-}Bu)_3$ dont le $pK_a = 11{,}40$. Les basicités mesurées sont en bon accord avec σ_p, σ^ϕ et ν ainsi qu'avec les potentiels d'ionisation des paires libres des triarylphosphines. D'une façon générale, les paramètres des spectres rmn du ^1H, du ^{13}C et du ^{31}P des phosphines libres et protonées ne sont pas en accord avec les pK_a.

[Traduit par le journal]

Introduction

Tertiary phosphines form stable complexes (1–4) with many main group Lewis acids as well as with transition metals in their various oxidation states. Due to very useful catalytic properties (5) of a number of phosphine complexes of transition metals, tertiary phosphines have become very widely studied ligands.

By analogy with the bonding of metal carbonyls, it has long been proposed that phosphines can act as σ donors as well as π acceptors (6–11). To test this hypothesis and to evaluate the electronic effects of phosphines on the properties of their complexes, tertiary phosphines with a variety of substituents on phosphorus have been synthesised and the electronic effects in their complexes have been investigated (1–4).

Tolman has proposed an empirical electronic parameter, ν, based on substituent group contributions, χ_i, derived from the CO stretching frequency belonging to the A_1 mode of the complexes $Ni(CO)_3PR_3$ (7). These are intended to be a quantitative measure of electronic effects.

Other workers (8–13) have used the inductive and mesomeric effects of the substituents attached to phosphorus to infer the electronic effects of phosphines. For example, the magnitude of $^1J(M\text{—}P)$ for complexes of tungsten(0) (8) and platinum(II) (9) with the phosphines PR_nPh_{3-n} (R = alkyl, Ph = phenyl) increases as *n* decreases but the opposite is true for some mercury(II) complexes (10). From these results it has been concluded (8–10) that the magnitude of $^1J(^{183}W\text{—}^{31}P)$ or $^1J(^{195}Pt\text{—}^{31}P)$ increases with decreasing basicity whereas the $^1J(^{199}Hg\text{—}^{31}P)$ values vary in the opposite manner. Using a Hammett-type relationship, Kabachnik and co-workers (14) have derived the substituent parameters σ^ϕ which have also been used as a measure of electronic effects of phosphines. It has been shown (15) that the reactivity of the complexes $IrCl(CO)L_2$ (L = triarylphosphine) toward oxidative addition of methyl iodide is linearly dependent upon the σ^ϕ values for the substituents at phosphorus.

Phosphines, like amines, are also Brønsted bases and the electronic effects of the substituents on the metal–phosphorus bond can be quantitatively measured in terms of the basicity of the phosphines toward a proton. It has been shown (16) that the half neutralisation potentials (HNP) for the water-insoluble phosphines in a non-aqueous solvent can be accurately correlated with their aqueous basicities. The pK_a values for a number of trialkyl phosphines have been determined by this method (16).

As part of a systematic investigation of the electronic and steric effects in the phosphine complexes of d^8 and d^{10} metals, the metal–phosphorus nuclear spin–spin couplings and/or metal–phosphorus stretching frequencies for the platinum(II) (17), mercury(II) (18), cadmium(II) (19), and silver(I) (20) complexes of tri-*tert*-butylphosphine,

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TABLE 1. Basicity, $^1H^a$ and ^{13}C nmr data

	Compound	pK_a	$^1J(P—H)^a$ (Hz)	$\delta(^1H)^a$ (ppm)	$^1J(P—C)$ (Hz)	$\delta(^{13}C)_{C_1}$ (ppm)	$\Sigma\sigma\phi^f$
I	$P(t\text{-}C_4H_9)_3$	11.40	443	5.21	−33.9	34.7^g	−4.65
II	$P(c\text{-}C_6H_{11})_3$	9.65	455	5.11	−28.8	30.6	−3.57
III	$P(4\text{-}(CH_3)_2NC_6H_4)_3$	8.65	494	8.27	−5.9	124.9	−3.51
IV	$P(4\text{-}CH_3OC_6H_4)_3$	4.57	494	8.32	−8.7	133.7	−2.22
V	$P(4\text{-}CH_3C_6H_4)_3$	3.84	509	8.33	-10.0^c	134.2^c	−2.16
VI	$P(3\text{-}CH_3C_6H_4)_3$	3.30	494	8.42	−12.3	137.1	−1.65
VII	$P(2\text{-}CH_3C_6H_4)_3$	3.08	491	8.83	-11.44^d	142.5^c	—
VIII	$P(C_6H_5)_3$	2.73	504	8.50	-12.51^e	137.4	−1.77
IX	$P(4\text{-}FC_6H_4)_3$	1.97	512^b	^{b}	−11.5	132.5	−0.96
X	$P(4\text{-}ClC_6H_4)_3$	1.03	499	8.44	−14.8	134.9	−0.87

[a] These values are for the protonated phosphines in CF_3CO_2H. All other nmr data are for the free phosphines in solution.
[b] $^1J(P—H)$ value taken from ^{31}P spectrum.
[c] Reference 38.
[d] Reference 37.
[e] Reference 36.
[f] Reference 14.
[g] Reference 39.

tricyclohexylphosphine, and a number of substituted triarylphosphines have been examined in this laboratory. The most significant finding of these investigations is that, contrary to conclusions arrived at from earlier studies, the magnitude of $^1J(M—P)$ for the *para* substituted triarylphosphine complexes of platinum(II) (17) as well as mercury(II) (18*g*) and cadmium(II) (19*b*) halides increase with increasing electron releasing power of the aryl group. It is therefore evident that $^1J(M—P)$ is not simply related to the electron-donating abilities of phosphines, which are more reliably measured by their basicities towards a proton. Thus, the dependence of the spectral parameters and other properties of the complexes can be evaluated quantitatively from the knowledge of the relative pK_a values of the phosphines. The pK_a values for the ten phosphines used in the nmr studies have been determined in the present work. Correlations between the phosphine basicity and the ^1H, ^{31}P, and ^{13}C nmr spectral parameters of the phosphines as well as the $^1J(^{31}P—^1H)$ values for the protonated phosphines have also been examined. The topic of substituent contributions to the ^{31}P chemical shift has been dealt with by others (41).

Results and discussion

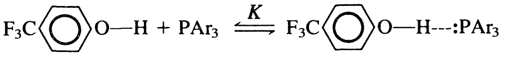
(*a*) *Basicities of phosphines*

The pK_a values for the ten phosphines examined in this study are given in Table 1 along with some of their ^1H and ^{13}C nmr data. The pK_a values for $P(c\text{-}C_6H_{11})_3$ and $P(4\text{-}CH_3OC_6H_4)_3$ are in good agreement with the values reported by Streuli (16*a*).

For the triarylphosphines the order of basicity is found to be the same as the order of the Hammett σ_p and σ_m parameters (21) for the substituents on the phenyl groups. $P(4\text{-}FC_6H_4)$ is found to be slightly more basic than $P(4\text{-}ClC_6H_4)_3$. This can be attributed to the more efficient conjugation of the non-bonding electrons on fluorine with the ring. In spite of the powerful inductive effect of fluorine, a significant amount of electron density is donated back to the ring. The three tritolylphosphines are all more basic than triphenylphosphine and their pK_a values occur within a small range. The higher basicities of $P(4\text{-}CH_3OC_6H_4)_3$ and $P(4\text{-}(CH_3)_2NC_6H_4)_3$ are expected because of the known electron donating abilities of the substituents. The two trialkylphosphines are significantly more basic than most of the triarylphosphines. They are, in fact, the most basic phosphines whose pK_a's have been measured to date. The very high value for $P(t\text{-}C_4H_9)_3$ compared to $P(c\text{-}C_6H_{11})_3$ is consistent with the greater electron-donating ability of the *t*-butyl groups.

It should be noted here that these results are not entirely consistent with some previous work, particularly with respect to the pK_a value for $P(4\text{-}ClC_6H_4)_3$. Goetz and Sidhu (22) measured the pK_a's of two classes of phosphines, $P(C_6H_5)_2(4\text{-}XC_6H_4)$ and $P(4\text{-}XC_6H_4)_3$, by a titration method using HCl in 80% ethanol/water. For the first class they found a good correlation between Hammett's constants and the measured pK_a values. The latter class gave the order of decreasing basicity ($P(4\text{-}CH_3OC_6H_4)_3 > P(4\text{-}ClC_6H_4)_3 > P(C_6H_5)_3$, which is different from ours.

Using a different technique, Hopkins and coworkers (23) also studied several symmetrical 4-substituted triarylphosphines. Using an infrared technique, they measured the equilibrium constant for eq. [1] by observing the free and H-bonded ν(OH) bands in dilute CS_2 solution.

[1] 

The rationale was that the more basic phosphines would H-bond more extensively to the phenol. This experiment gave an order of decreasing basicity of $P(4\text{-}CH_3OC_6H_4)_3 \gg P(4\text{-}CH_3C_6H_4)_3 > P(4\text{-}ClC_6H_4)_3 > P(C_6H_5)_3$.

While it is difficult to criticise the methodology of the former study, the latter is open to various interpretations. One possible explanation for the deviation of Hopkins' order from ours is that the substituents which are themselves capable of H-bonding (—Cl and —OCH_3) are doing so and raising the apparent basicities of the phosphines. In support of our study is one in which the equilibrium in the reaction of phosphines and tritylperchlorate (eq. [2]) was

[2] $$Ar_3P + Ar_3{}^+C + ClO_4{}^- \rightleftharpoons Ar_3P^+\text{—}CAr_3 + ClO_4{}^-$$

studied (24). The more basic phosphines shifted the reaction to the right to give an order of decreasing basicity:

$$P(4\text{-}CH_3C_6H_4)_3 > P(C_6H_5)_3 > P(4\text{-}ClC_6H_4)_3$$

Also in support of our work, and more directly comparable, is a protonation study by Grim and Yankowsky (11). They were able to qualitatively assign basicities to eighteen triarylphosphines based on whether the doublet due to the phosphonium proton could be seen by ^1H nmr after bubbling HBr(g) through CH_2Cl_2 solutions of the phosphines. Their results are consistent with our study; the phosphonium proton was most easily observed with the most basic phosphines.

Correlations of the basicities of phosphines with Hammett's σ_{mp} parameters (22) and to Tafts σ^* parameters (16*b*) have been demonstrated. Correlations using these constants are not possible, however, when the groups attached to phosphorus are mixed alkyl–aryl or are not organic. The basicities of these other phosphines can be correlated with Kabachnik's σ^ϕ constants (14). These values are proportional to Hammett's σ constants for substituted aromatic groups but also include a wide range of alkyl, alkoxy, and halide groups. Because these constants are derived from the ionisation of phosphorus acids they should, at least in principle, be better constants to use with phosphorus compounds.

The correlation between pK_a and σ^ϕ for the phosphines in this study is excellent (see Fig. 1). Mastryukova and Kabachnik (14) have pointed out that the data of Henderson and Streuli fall on one line when σ^ϕ is used rather than the three lines obtained when pK_a is plotted vs. σ^* (16*b*).

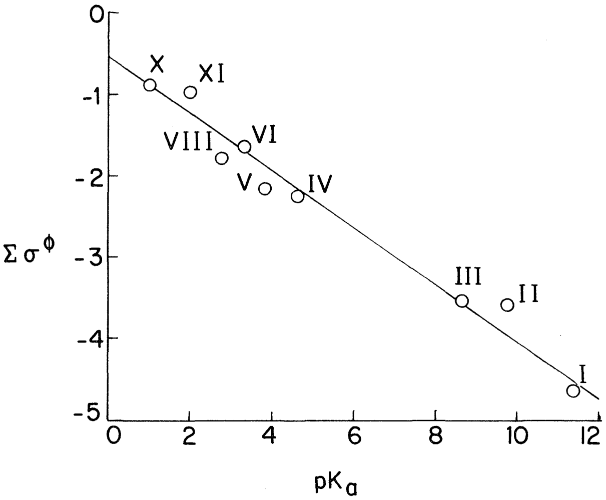


FIG. 1. Plot of Kabachnik's $\Sigma\sigma^\phi$ vs. pK_a. Numbers correspond to those in the tables.

$$\Sigma\sigma^\phi = -0.351pK_a - 0.540,$$

$$r = -0.986.$$

Tolman has proposed constants for the phosphines, χ_i, which also reflect the changes in basicity very well (7*a*). In his paper Tolman gives a plot of χ_i vs. σ^ϕ which shows significant deviation from linearity in the region of low basicity, particularly in the region where the phosphites are found. As shown in Fig. 2, for the phosphine used in this study the correlation between pK_a and χ_i is linear, probably because the range of basicities of our phosphines is smaller.

It is reasonable that the phosphorus lone pair ionisation potential (IP) should reflect the variations with ring substitution that we have seen by these other techniques. The lone pair IP of several 4-substituted triarylphosphines have been determined recently by ultraviolet photo-electron spectroscopy. Weiner and Lattman (25) found a good correlation between lone pair IP and σ_p but point out that this implies that there are no major changes in hybridisation at phosphorus through the series. Another study (26) corroborates this by showing that while there may be good correlations within a series of closely related phosphines, it is not a good technique for determining the relative basicities of very different phosphines such as PCl_3 and $(P(C_6H_5)_3$. Indeed, while the IP of all the triarylphosphines used in this study correlate well with pK_a (Fig. 3), the point for $P(t\text{-}C_4H_9)_3$ is far from the line. The C—P—C angle in the triarylphosphines is probably close to the 103.0° of $P(C_6H_5)_3$ (27) while the angle in $P(t\text{-}C_4H_9)_3$ is larger at 109° (26, 28).

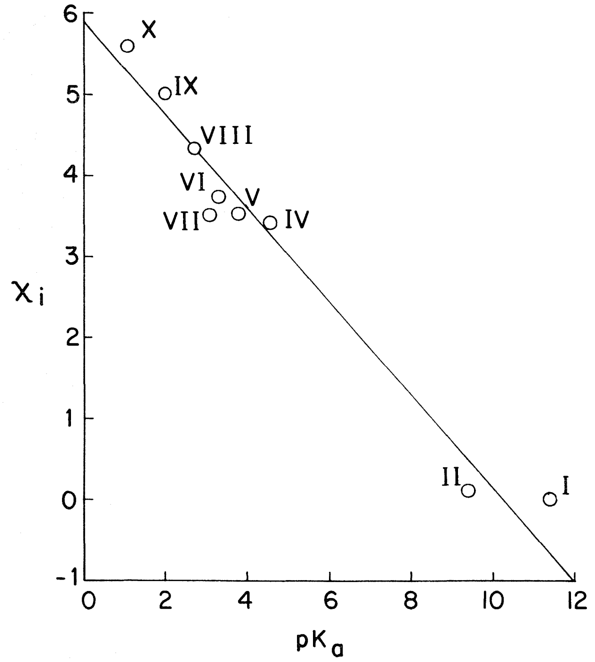


FIG. 2. Plot of Tolman's χ_i parameters vs. pK_a. Numbers correspond to those in the tables.

$\chi_i = -0.577\mathrm{p}K_a + 5.90,$

$r = -0.960$

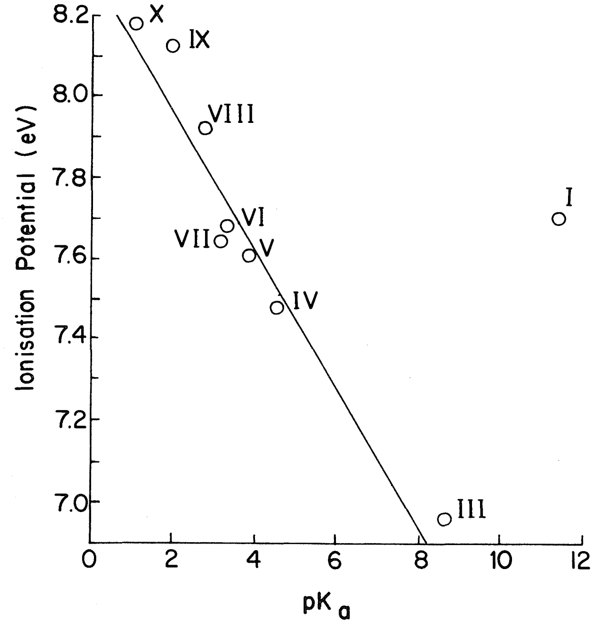


FIG. 3. Plot of phosphorus lone pair ionisation potential vs. pK_a. Numbers correspond to those in the tables. The point for *I* is not included in the regression line.

$\mathrm{IP} = -0.163\mathrm{p}K_a + 8.29,$

$r = 0.978$

(b) Nuclear magnetic resonance data

(i) ^{1}J(P—H) in the protonated phosphines

Previous workers have generated the phosphonium ions by dissolving the phosphines in very strongly acid media such as 100% H_2SO_4 (12) or HSO_3F (13) or by bubbling HBr(g) through solutions of the phosphines in CH_2Cl_2. We find that the ions can be observed easily in trifluoroacetic acid solution. The nmr data for these ions are given in Table 1.

The coupling constants decrease slightly in the triaryl series with increasing basicity as do the chemical shifts, but the correlation is poor. In light of the wide range of basicity in this series the small range of ^1J(P—H) is surprising. The two trialkylphosphines give coupling constants that are significantly lower than the others. However, these data are consistent with those from previous studies (11–13); some selected data are presented in Fig. 4. It can be seen clearly that ^1J(P—H) decreases with increasing basicity (decreasing $\Sigma\sigma^\phi$) of the phosphine or phosphite. Put it in another way, ^1J(P—H) increases with increasing electronegativity of the substituents in a reasonably smooth manner. This trend is indeed well known for ^1J(C—H) in various organic compounds. For example, ^1J(C—H) decreases in the series $HCF_3 > HCCl_3 > HCBr_3 > HCI_3$. These results are consistent with Bent's rule (29) which states that *p* character tends towards the orbitals with the most electronegative substituents. Because the sum of *s* character of the carbon orbitals must be exactly 1,

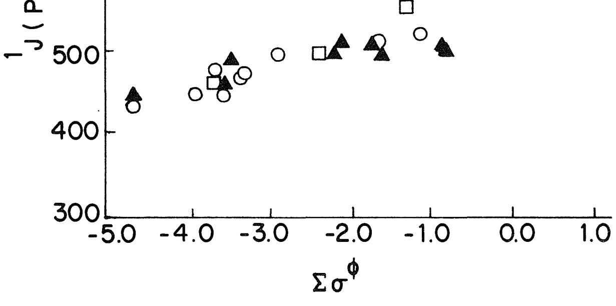


FIG. 4. Plot of ^1J(P—H) of the protonated phosphines vs. pK_a. ▲, this study; ○, ref. 14, □, ref. 13.

the C—H bond will have more *s* character in HCF_3 than in $HCCl_3$. The higher coupling constant implies that the Fermi contact mechanism is dominant in determining these coupling constants (30, 31). Extension of this reasoning to organophosphines is probably sound because no multiple bonding between phosphorus and hydrogen is possible and it has generally been accepted that M—H coupling is explained by this mechanism (32). Supporting this view is the observation that ^1J(P—H) correlates well with the calculated charges on phosphorus and hydrogen in some protonated phosphites (33).

(ii) ^{1}J*(P—C) in the free phosphines*

The observed trend in ^1J(P—C) is not as easily explained. The Fermi contact term, although important, has been found to contribute less as the coupled atoms become heavier and where there is multiple bonding between them (34). If it is assumed that the sign of the coupling constant is merely a label defining the origin of the coupling and that it is the magnitude of the coupling constant that is important, then the trend in ^1J(P—C) vs. pK_a is not explicable in terms of changes in the Fermi contact term. Rehybridisation of phosphorus in accordance with Bent's rule would increase the *s* character of the P—C bond with increasing basicity of the phosphine thus giving a higher ^1J(P—C). We see the opposite trend in the triaryl phosphine data in Fig. 5. These changes in the C—P—C angle are likely to be small, if indeed they do exist. So far, there are not enough crystallographic data to know. Much larger changes in hybridisation can be forced by including the phosphorus atom in a heterocyclic ring or by replacing an aryl group by cyclohexyl or *t*-Bu. It has been found that changes in ^1J(P—C) are consistent with rehybridisation at phosphorus and the Fermi contact mechanism in such ring systems (35).

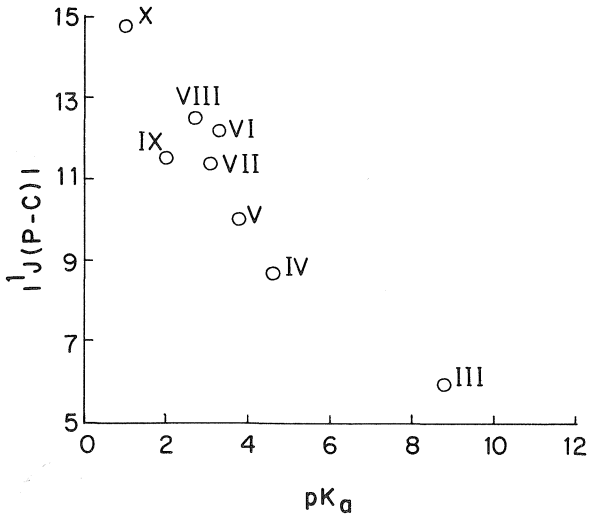


FIG. 5. Plot of |^1J(P—C)| vs. pK_a for the triarylphosphines. Numbers correspond to those in the tables.

What can be learned from this is that the interpretation of coupling constants is by no means easy. The other factors in the Fermi contact expression, the electron density at the nucleus and the triplet excitation energy, can only be guessed at and the contributions of the orbital and dipolar mechanisms are unknown. It is likely that several contributions to the coupling constant are changing through the aryl phosphine series and not all in the same direction, thus, giving a correlation of ^1J(P—C) with pK_a which probably means very little by itself.

Conclusions

We have shown that substituents on the phenyl rings of triarylphosphines can bring about large changes in the basicities of these phosphines. They should be useful for studies where electronic changes without significant concurrent steric changes are desired. The measured basicities correlate well with σ_p, σ^ϕ, and v as well as with the lone pair ionisation potentials for members of a series of similar phosphines. Generally, the nmr spectral parameters do not correlate well with the measured basicities and do not provide an alternate method of determining basicities. Of all the methods devised to date the nitromethane titration appears to be the most consistent and reasonable method for the measurement of basicities of phosphines.

Experimental section

(a) Materials

Triphenylphosphine from Eastman Kodak was recrystallised twice from hot ethanol and dried *in vacuo*. Tris(4-dimethylaminophenyl) phosphine from Strem Chemicals was purified by recrystallisation from hot benzene under N_2. Tricyclohexylphosphine was used as received from Pressure Chemical Co. Tri-*tert*-butylphosphine was prepared as previously reported (40). All other phosphines were prepared as described in (*b*). Purity of each phosphine was established by melting point and ^{1}H and ^{31}P nmr spectral measurements and, except for tri-*tert*-butylphosphine and tricyclohexylphosphine, by elemental analysis. Trifluoroacetic acid from Eastman Kodak was distilled onto molecular sieves and stored in a desiccator. Reagent grade nitromethane and perchloric acid were used as received.

(b) Synthesis of triarylphosphines

The preparation of $P(4\text{-}ClC_6H_4)_3$ is described as a representative procedure for the preparation of the triarylphosphines. All glassware was oven-dried and flushed with dry dinitrogen before use. The starting material, 1-bromo-4-chlorobenzene (100 g, 0.52 mol) was dissolved in ~ 100 mL of reagent grade THF from a freshly opened bottle. This solution was slowly added to a 500 mL 3-necked flask containing magnesium turnings (12.7 g, 0.52 mol) and THF (~ 50 mL). The reaction started spontaneously after about 2–3 min. The reagent solution was added continu-

TABLE 2. Analytical data[a]

	Compound	Melting point (°C)	C		H		$\delta(^{31}P)$ (ppm)	$\delta(^1H)_{CH_3}$[b] (ppm)
			Calcd.	Found	Calcd.	Found		
I	$P(t\text{-}C_4H_9)_3$	27–29	—	—	—	—	56.7	3.12[c]
II	$P(c\text{-}C_6H_{11})_3$	76–77	—	—	—	—	8.8	—
III	$P(4\text{-}(CH_3)_2NC_6H_4)_3$	265–270	73.6[d]	73.7	7.7	7.4	−11.7	3.07
IV	$P(4\text{-}CH_3OC_6H_4)_3$	135–137	71.6	71.0	6.0	6.0	−10.6	3.78
V	$P(4\text{-}CH_3C_6H_4)_3$	145–148	82.9	82.7	7.0	7.0	−8.3	2.34
VI	$P(3\text{-}CH_3C_6H_4)_3$	103–104	82.9	83.2	7.0	6.7	−5.3	2.29
VII	$P(2\text{-}CH_3C_6H_4)_3$	125–127	82.9	82.9	7.0	6.9	−27.8	2.38
VIII	$P(C_6H_5)_3$	80	82.4	82.2	5.8	5.9	−6.3	—
IX	$P(4\text{-}FC_6H_4)_3$	80–81	68.4	68.5	3.8	3.6	−9.3[e]	—
X	$P(4\text{-}ClC_6H_4)_3$	100–101	59.1	59.4	3.3	3.3	−8.7	—

[a] The analytical data are in agreement with those in ref. 41.

[b] These methyl shifts are included because they are diagnostic and show significant shifts on coordination of the phosphine. All the aryl phosphines showed aromatic multiplets around $\delta = 7$. The spectrum of II was an unresolved and very complex multiplet between $\delta = 1.0$ and $\delta = 3.0$.

[c] $^3J(P\text{—}H) = 9.5$ Hz.

[d] %N = 10.7 (calcd.) 11.2 (found).

[e] Quartet. $^5J(P\text{—}F) = 4.4$ Hz.

ously at a rate necessary to maintain reflux. The total time of addition was about 1 h. Using the same dropping funnel, a solution of PCl_3 (23.9 g, 0.17 mol, 15.2 mL) in 50 mL THF was prepared and added slowly, also at a rate necessary to maintain reflux. Up to this point all reactions were done under dry nitrogen. Enough water was added to produce two layers in the flask and the organic layer was removed and filtered. The aqueous portion was extracted twice with 50 mL portions of diethyl ether which were also filtered and added to the first organic portion. The aqueous portion was discarded and the organic solution was evaporated. The residue, which had a definite orange colour, was recrystallised from hot ethanol repeatedly until a white crystalline product was obtained. Elemental analyses were performed by Guelph Chemical Laboratory, Guelph, Ontario. Analytical data are given in Table 2 which also contains the $^{31}P\text{—}\{^1H\}$ and ^1H nmr data.

(c) *Determination of basicities*

The method of Streuli (16) was modified to suit the equipment and materials available in our laboratory. A solution of $HClO_4$ (0.2 *M*), prepared by adding reagent grade 70% $HClO_4$ (8.4 mL) to CH_3NO_2 (500 mL), was deoxygenated by bubbling dry N_2 through it for 30 min. Titrations were performed using a 5 mL self-filling burette attached to a source of N_2. The phosphines (~ 1 mmol per determination) were dissolved in CH_3NO_2 (100 mL) and the titration was followed using a Chemtrix digital pH–mV meter with a combination glass–calomel electrode. The best results were obtained when the electrode was allowed to sit in nitromethane a few hours before the titrations were performed. The endpoint was determined from a derivative plot and the half neutralisation potential (HNP) was recorded. Three separate determinations were made for each phosphine. Triphenylphosphine was used as a standard instead of diphenylguanidine. The difference, HNP(triphenylphosphine) − HNP(phosphine), was calculated. The ΔHNP used by Streuli is merely this value plus 573 mV which is the ΔHNP of triphenylphosphine when diphenylguanidine is used as a reference. This new value can now be used in the equation

$$pK_a = 10.12 - 0.0129(\Delta HNP)$$

where

$$pK_a = -\log_{10} [H^+][PR_3]/[HPR_3^+]$$

The value HNP(triphenylphosphine) was determined daily before the titrations. Tri-*tert*-butylphosphine, tricyclohexylphosphine, and tris(4-dimethylaminophenyl)phosphine were titrated under an atmosphere of oxygen-free nitrogen using deoxygenated solvent. The others were titrated in air. Smaller amounts (~ 0.3 mmol) of tricyclohexylphosphine and tris(4-dimethylaminophenyl)phosphine were used because of their low solubility in nitromethane.

Because of the possible ambiguity about the site of protonation of $P(H\text{-}(CH_3)_2NC_6H_4)_3$ the titration was continued past the first endpoint. A second equivalence point was found at four times the volume of titrant as for the first. Clearly the first endpoint was from the protonation of the phosphorus atom and the second was from the protonation of the nitrogen atoms.

The reproducibility of the titrations was equivalent to ± 0.05 pK_a units.

(d) *Nuclear magnetic resonance measurements*

(i) *Measurements of* $^1J(P\text{—}H)$

The phosphonium ions were generated by dissolving the phosphines in dry trifluoroacetic acid to give clear colourless solutions. High phosphine concentrations tended to promote exchange of the phosphonium protons so that solutions were no more concentrated than necessary to observe the doublet due to the phosphonium proton. The $^1J(P\text{—}H)$ values for the phosphonium ions of all the phosphines except tris(4-fluorophenyl)phosphine were determined from their ^1H nmr spectra measured at ambient temperature with a Varian T-60 nmr spectrometer using TMS as the internal reference. The $^1J(P\text{—}H)$ value for protonated tris(4-fluorophenyl)phosphine was obtained from its ^{31}P nmr spectrum run on a Bruker WP-60 FT nmr spectrometer using 85% H_3PO_4 as external reference.

(ii) *Spectra of the free phosphines*

All spectra but two (^{13}C of **VI** and **X**) were recorded on a Bruker WP-60 FT nmr spectrometer. The other two spectra were run on a Bruker WH-400 FT nmr spectrometer to remove the peak overlap which made assignments impossible in the low field spectra. The ^1H and ^{13}C spectra were run in $CDCl_3$ (aryl phosphines) or C_6D_6 (alkyl phosphines) using the deuterium lock and internal TMS as a reference. All ^{31}P spectra were measured on concentrated CH_2Cl_2 solutions to which 10% v/v C_6D_6 was added to provide a deuterium lock. A capillary of 85% H_3PO_4 was used as an external reference. ^{13}C and ^{31}P spectra were proton decoupled using a broad band decoupler. All shifts are reported in the same sense; that is, positive shifts are to high frequency of the reference.

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