$[Na.C221]^+$ is substantially more stable than $[Na.C22C_2]^+$.

## Conclusion

The variation of the stability of $[M.C22C_2]^+$ with $M^+$ in the sequence $Li^+ < Na^+ > K^+ > Cs^+$ is consistent with the flexible structure of clamlike $C22C_2$ allowing the angle between its two jaws hinged about the $>NCH_2CH_2N<$ moiety to vary with the size of the complexed $M^+$ such that optimum bonding distances and a minimization of strain are achieved in $[Na.C22C_2]^+$. Although this metal ion selection mode of $C22C_2$ differs from that of less flexible cryptands, the magnitudes of the stability constants and kinetic parameters are within the range arising from the interplay of the effects of the number of donor atoms and cryptand flexibility, which produce variations in cryptate stability and lability generally.

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Contribution from the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

# Bidentate Phosphine Basicities As Determined by Enthalpies of Protonation

John R. Sowa, Jr., and Robert J. Angelici*

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Enthalpies for both the first ($\Delta H_{HP1}$) and the second ($\Delta H_{HP2}$) protonations of the phosphorus donors in bidentate phosphines have been determined by titration calorimetry using $CF_3SO_3H$ in 1,2-dichloroethane solvent. The $\Delta H_{HP1}$ values for the series $Ph_2P(CH_2)_nPPh_2$, $n$ = 1–6, range from $-22.0 \pm 0.1$ kcal mol$^{-1}$ for $n$ = 1 to $-25.2 \pm 0.1$ kcal mol$^{-1}$ for $n$ = 6. The $\Delta H_{HP2}$ values also become more exothermic from −14.9 ● 0.2 to −24.9 ● 0.1 kcal mol$^{-1}$ with increasing alkyl chain length. The $\Delta H_{HP1}$ and $\Delta H_{HP2}$ values for other bidentates, $Ph_2P(bridge)EPh_2$ (E = P, bridge = *cis*-CH═CH, *trans*-CH═CH, 1,2-$C_6H_4$; E = As, bridge = $CH_2CH_2$) and $Me_2PCH_2PMe_2$, have also been determined. Correlations of $\Delta H_{HP1}$ and $\Delta H_{HP2}$ with the corresponding p$K_{a1}$ and p$K_{a2}$ values taken from the literature are presented.

## Introduction

Bidentate and monodentate phosphines are common ligands in organometallic and coordination chemistry.[1] Much effort has been directed toward understanding the effects of monodentate phosphines on properties of metal complexes. For example, Giering,[2a] Poë,[2b] and co-workers have recently introduced an approach to the quantitative analysis of ligand effects (QALE) using the steric and electronic properties of phosphorus(III) ligands. Relatively few studies, however, have focused on the relationship between the properties of bidentate ligands and the properties of their metal complexes.[3,4]

Previously, Bush and Angelici[5] measured the enthalpies of protonation ($\Delta H_{HP}$, eq 1) of several aryl-, mixed alkyl-/aryl-, and alkylphosphines with 0.1 M $CF_3SO_3H$ in 1,2-dichloroethane (DCE) solution. These $\Delta H_{HP}$ values are a quantitative measure

$$PR_3 + CF_3SO_3H \xrightarrow[25.0\ °C]{DCE} HPR_3^+CF_3SO_3^-;\quad \Delta H_{HP} \qquad (1)$$

of the basicities or $\sigma$-donor abilities of these monodentate phosphines. In this paper, we report the basicities of several bidentate phosphines as determined by their enthalpies of protonation with 0.1 M $CF_3SO_3H$ in DCE. For the dibasic phosphines, which are listed with their abbreviations in Table I, $\Delta H_{HP1}$ represents the heat liberated during the addition of the first equivalent of acid, while $\Delta H_{HP2}$ is the enthalpy of reaction for the addition of a second equivalent of acid. The protonation reactions occurring in these solutions are given in eqs 2 and 3 but do not necessarily represent

$$\overset{\frown}{P\ P} + CF_3SO_3H \xrightarrow[25.0\ °C]{DCE} H\overset{\frown}{P\ P}{}^+CF_3SO_3^- \qquad (2)$$

$$H\overset{\frown}{P\ P}{}^+CF_3SO_3^- + CF_3SO_3H \xrightarrow[25.0\ °C]{DCE} H\overset{\frown}{P\ P}H^{2+}(CF_3SO_3^-)_2 \qquad (3)$$

$\Delta H_{HP1}$ and $\Delta H_{HP2}$, respectively, as will be discussed. The results of these studies give a quantitative measure ($\Delta H_{HP1}$ and $\Delta H_{HP2}$) of the $\sigma$-donor properties of bidentate phosphine ligands.

**Table I.** $\Delta H_{HP1}$, $\Delta H_{HP2}$ and p$K_{a1}$, p$K_{a2}$ Values for Bidentate Phosphines

| phosphine | $-\Delta H_{HP1}$,[a] kcal mol$^{-1}$ | p$K_{a1}$[b] | $-\Delta H_{HP2}$,[c] kcal mol$^{-1}$ | p$K_{a2}$[b] |
|---|---|---|---|---|
| $Ph_2PCH_2PPh_2$ (dppm) | 22.0 (±0.1) | 3.81 | 14.9 (±0.2) | −2.73 |
| $Ph_2P(CH_2)_2PPh_2$ (dppe) | 22.8 (±0.2) | 3.86 | 20.2 (±0.1) | 0.99 |
| $Ph_2P(CH_2)_3PPh_2$ (dppp) | 23.4 (±0.1) | 4.50 | 22.4 (±0.3) | 2.53 |
| $Ph_2P(CH_2)_4PPh_2$ (dppb) | 24.6 (±0.1) | 4.72[f] | 23.8 (±0.2) | 4.28[f] |
| $Ph_2P(CH_2)_5PPh_2$ (dppent) | 24.8 (±0.2) | 4.84[f] | 24.5 (±0.1) | 4.67[f] |
| $Ph_2P(CH_2)_6PPh_2$ (dpph) | 25.2 (±0.1) | 5.05[f] | 24.9 (±0.1) | 4.89[f] |
| *cis*-$Ph_2P(CH{=}CH)PPh_2$ (*cis*-dppv) | 19.9 (±0.3) | 2.27 | 10.0 (±0.2) | |
| *trans*-$Ph_2P(CH{=}CH)PPh_2$ (*trans*-dppv) | 21.7 (±0.2) | 2.74 | 12.7 (±0.1) | |
| $Ph_2P(1,2\text{-}C_6H_4)PPh_2$ (dppbz) | 21.3 (±0.1) | 2.91[f] | 10.7 (±0.3) | |
| $Ph_2P(CH_2)_2AsPh_2$ (arphos) | 23.2 (±0.4) | 3.96[f] | 8.2 (±0.1) | |
| $Me_2PCH_2PMe_2$ (dmpm) | 31.0 (±0.3) | 8.24[f] | 25.8 (±0.2) | |
| $Et_2P(CH_2)_2PEt_2$ (depe) | 31.3[f] | 8.41[b] | | 5.04[b] |
| ($p$-$CF_3C_6H_4)_3P$ | 13.6 (±0.2)[d] | −1.32[f] | | |
| $PPh_3$ | 21.2 (±0.1)[d,e] | 2.73[e] | | |
| $PPh_2Me$ | 24.7 (±0.0)[d,e] | 4.59[e] | | |
| $PMe_3$ | 31.6 (±0.2)[d,e] | 8.65[e] | | |

[a] For protonation with 1 equiv of $CF_3SO_3H$ in DCE solvent at 25.0 °C. [b] Reference 10. [c] For addition of a second equivalent of $CF_3SO_3H$ in DCE solvent at 25.0 °C. [d] $\Delta H_{HP}$, eq 1. [e] Selected from ref 5. [f] Calculated from eq 7.

The studies presented herein are part of a program aimed at determining the quantitative effects of ligands on the basicities of transition-metal complexes (eq 4). We have already reported[6]

$$ML_x + CF_3SO_3H \xrightarrow[25.0\ °C]{DCE} HML_x^+CF_3SO_3^-;\quad \Delta H_{HM} \qquad (4)$$

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a study of the effect of methyl groups in the cyclopentadienyl ligand in Cp′Ir(COD) (Cp′ = $C_5Me_xH_{5-x}$, $x$ = 0, 1, 3–5; COD = 1,5-cyclooctadiene) on the iridium metal basicity. Forthcoming results will describe the relative effects of bidentate and monodentate ligands on transition-metal complex basicities.

## Experimental Section

The phosphine ligands used in these studies and their abbreviations are given in Table I. The following were purchased from Aldrich: dppm, *cis*-dppv, *trans*-dppv, dppent, and dpph. Dppe, dppbz, dppp, dppb, dmpm, and tris(*p*-(trifluoromethyl)phenyl)phosphine were purchased from Strem. Arphos was obtained from Pressure Chemical Co. Dppp was purified by dissolving ~1.2 g of the compound in 6 mL of $CH_2Cl_2$ and filtering through 1 cm of Celite on a medium porosity frit. The resulting solution was then evaporated to ~3 mL, and 10 mL of EtOH (95%) was added. The mixture was evaporated under vacuum until crystallization occurred. Filtration followed by a 2 × 2 mL cold EtOH wash and drying under vacuum gave white crystalline needles. Arphos and dpph were recrystallized by dissolving the compound in a minimum of $C_6H_6$, filtering, and adding hexanes (~2 × volume). The solution was cooled to 10 °C for 12 h. The resulting precipitate was collected by filtration, washed with 2 × 2 mL of cold hexanes, and dried under vacuum. Dppe was recrystallized from hot EtOH (95%) and dried under vacuum. All other compounds were used as received.

The calorimetric titration procedure was similar to that previously described.[5,6] The titrations were performed under an atmosphere of argon. Typically a run consisted of three sections: initial heat capacity calibration, titration (at 25.0 °C), and final heat capacity calibration. Each section was preceded by a base-line-acquisition period. For the determination of $\Delta H_{HP1}$, the titration period involved the addition of ~1.2 mL of a 0.1 M $CF_3SO_3H$ solution (standardized to a precision of ±0.0002 M) in DCE at a constant rate during a 3-min time period to 50 mL of a ~2.6 mM solution of the phosphine (~10% excess) in DCE at 25.0 °C. To obtain $\Delta H_{HP2}$, slightly more than 1 equivalent of $CF_3SO_3H$ (0.1 M, ~0.105 mmol) was added to a 50 mL solution of the bidentate phosphine (~0.100 mmol). The second equivalent of acid was then added (0.095 mmol) at a constant rate during an ~2-min time period to titrate at 25.0 °C the remaining unprotonated phosphine. The reaction enthalpies were corrected for the heat of dilution ($\Delta H_{dil}$) of the acid in DCE (~0.2 kcal mol$^{-1}$).[6]

The enthalpy values reported in Table I are averages of at least four titrations and as many as eight. At least two different standardized acid solutions were used for the titrations of each compound. The error is reported as the average deviation from the mean.

## Results

The $\Delta H_{HP1}$ values[7] (Table I) range from −19.9 kcal mol$^{-1}$ for *cis*-dppv to −31.0 kcal mol$^{-1}$ for dmpm and are comparable to the range of $\Delta H_{HP}$ values for the monodentate $PR_3$ compounds presented previously (−17.9 kcal mol$^{-1}$ for $(p\text{-ClC}_6H_4)_3P$ to −36.6 for $(t\text{-Bu})_3P$).[5] However, the $\Delta H_{HP2}$ values[7] for the smaller chelates, for example, dppm (−14.9 kcal mol$^{-1}$), are much less exothermic than any values we have yet reported.[5,6] Nevertheless, all titration curves were linear, indicating stoichiometric reaction of the acid with the neutral and monoprotonated species. The pre- and posttitration slopes were normal, indicating that there were no side reactions.

The low dielectric constant ($\epsilon$ = 10.36)[8] of DCE suggests that the products formed in eqs 2 and 3 probably occur as ion pairs. Dissociation of these ion pairs and autoprotolysis and dimerization of the acid are other reactions that may occur in nonpolar solvents such as DCE. An analysis of these factors was presented in the monodentate phosphine basicity study;[5] it was concluded that they contribute a total of ~0.3 kcal mol$^{-1}$ to the $\Delta H_{HP}$ value. Presumably these reactions also contribute negligibly to the $\Delta H_{HP1}$ and even the weakly exothermic $\Delta H_{HP2}$ values in this study.

The $\Delta H_{HP}$ value (eq 1) of the monodentate, weakly basic $(p\text{-CF}_3C_6H_4)_3P$ was determined to be −13.6 kcal mol$^{-1}$.

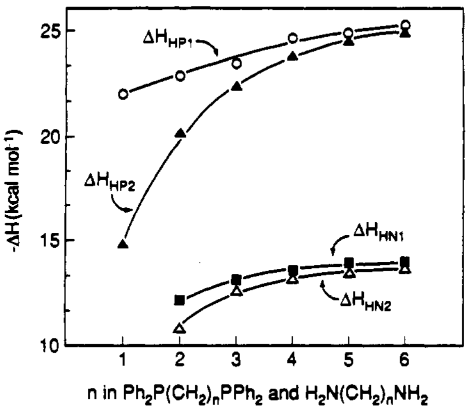

Figure 1. Plot of $\Delta H_{HP}$ vs $n$ of $Ph_2P(CH_2)_nPPh_2$ (upper two curves) and $\Delta H_{HN}$ vs $n$ of $H_2N(CH_2)_nNH_2$ (lower two curves). $\Delta H_{HN}$ values are taken from ref 11a.

## Discussion

**$\Delta H_{HP1}$ and $\Delta H_{HP2}$ Values for the Series $Ph_2P(CH_2)_nPPh_2$.** The $-\Delta H_{HP1}$ values for the $Ph_2P(CH_2)_nPPh_2$ compounds ($n$ = 1–6) increase with increasing chain length (Figure 1) but level off at a value of approximately 25.0 kcal mol$^{-1}$. This trend can be explained by assuming that the $PPh_2$ group is electron-withdrawing relative to an alkyl chain. Linear free energy analyses[9] further indicate the electron-withdrawing character of the $PPh_2$ group (Hammett constant: for $PPh_2$, $\sigma_p$ = 0.19; for $CH_3$, $\sigma_p$ = −0.17). Thus, as the alkyl chain is lengthened and the electron-withdrawing $PPh_2$ group is moved away from the site of protonation, the phosphorus becomes more basic. Beyond approximately $n$ = 4, an increase in the alkyl chain length does not change $\Delta H_{HP1}$. At this point, $\Delta H_{HP1}$ is about −25.0 kcal mol$^{-1}$, which is, within experimental error, the same as $\Delta H_{HP}$ (−24.7 kcal mol$^{-1}$) of $PPh_2Me$ (Table I).

The $-\Delta H_{HP2}$ values also increase as the alkyl chain length increases; they level off at about 24.7 kcal mol$^{-1}$ for the higher $n$ values (Figure 1). A comparison of $\Delta H_{HP1}$ (−22.0 kcal mol$^{-1}$) and $\Delta H_{HP2}$ (−14.9 kcal mol$^{-1}$) for dppm shows that $PPh_2H^+$ is a much stronger electron-withdrawing group than $PPh_2$. However, the effect of $PPh_2H^+$ is rapidly attenuated to the point that at large $n$ values both $\Delta H_{HP1}$ and $\Delta H_{HP2}$ reach the same limiting value of approximately −24.8 kcal mol$^{-1}$, which is essentially the same as the value for $PPh_2Me$ (−24.7 kcal mol$^{-1}$).

Thus, for the $n$ = 5 and 6 ligands, dppent and dpph, the basicities of the P donors are the same regardless of whether the other end of the ligand is protonated or not. That is, the basicity of one end of the ligand is not influenced by the form of the other end, $PPh_2$ or $PPh_2H^+$.

A consequence of this is that during titration with the first equivalent of acid, both mono- and diprotonated $P^\frown P$ are probably formed (eqs 2 and 3). Thus, $\Delta H_{HP1}$ does not simply correspond to the enthalpy of eq 2. To determine to what extent $\Delta H_{HP1}$ corresponds to eq 2 for the bidentate phosphines, we estimated the amounts of $P^\frown P$, $HP^\frown P^+$, and $HP^\frown PH^{2+}$ present in solution after the addition of 1 equiv of $CF_3SO_3H$. Previously, aqueous $pK_{a1}$ and $pK_{a2}$ values (Table I)[10] for several bidentate phosphines were determined from glass electrode potentials (ΔHNP) at half neutralization with $HClO_4$ in $CH_3NO_2$; these ΔHNP values were then converted to $pK_a$ values in water. Assuming the relative $pK_{a1}$ and $pK_{a2}$ values (Table I)[10] for dppm, dppe, and dppp measured in $CH_3NO_2$ to be the same in DCE, we can calculate using eq 5 the concentrations of $P^\frown P$, $HP^\frown P^+$, and $HP^\frown PH^{2+}$ in the titration

$$K = K_{a1}/K_{a2} = [P^\frown P][HP^\frown PH^{2+}]/[HP^\frown P^+]^2 \qquad (5)$$

solutions after 1 equiv of $CF_3SO_3H$ has been added. For the

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(7) The reactions are performed under conditions that approximate the standard state of reactions in dilute solution, which is defined as a hypothetical ideal solution of unit molality where the partial molar enthalpy of the solute is the same as in an infinitely dilute real solution. Thus, $\Delta H_{HP1,2} \cong \Delta H^\circ_{HP1,2}$.

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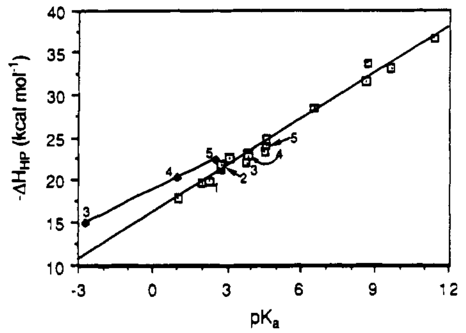

**Figure 2.** Plot of $\Delta H_{HP1}$ vs $pK_{a1}$ (⊡) and $\Delta H_{HP2}$ vs $pK_{a2}$ (◆) for bidentate and monodentate phosphines. Numbers refer to the following compounds: (1) *cis*-dppv; (2) *trans*-dppv; (3) dppm; (4) dppe; (5) dppp. Points (⊡) not labeled are monodentate ($PR_3$) $\Delta H_{HP}$ values from ref 5. The $pK_{a1}$ and $pK_{a2}$ values are taken from ref 10.

addition of 1 equiv of $CF_3SO_3H$ to 50 mL (the 1.2-mL volume change is negligible) of 2.6 mM $P^\frown P$ ($1.2 \times 10^{-4}$ mol), the percentage of the ligand in the monoprotonated form ($HP^\frown P^+$) is >99% for dppm, 92% for dppe, and 75% for dppp. Thus, for dppm, dppe, and probably *cis*- and *trans*-dppv, where $pK_{a2}$ is too low to be measured[10] in $CH_3NO_2$ (<0.0 $pK_a$ units), the $\Delta H_{HP1}$ values correspond to protonations of $P^\frown P$ to form primarily $HP^\frown P^+$ (eq 2), and $\Delta H_{HP2}$ values correspond primarily to protonations of $HP^\frown P^+$ to form $HP^\frown PH^{2+}$ (eq 3). The $\Delta H_{HP1}$, $\Delta H_{HP2}$ values for dppbz and arphos probably also fall into this category; however, $pK_{a1}$ and $pK_{a2}$ values for these ligands have not been published. Because $pK_{a1}$ (8.41) is substantially greater than $pK_{a2}$ (5.04) for depe[10] the same will almost certainly be true for dmpm as well; therefore, the $\Delta H_{HP1}$ (−31.0 kcal $mol^{-1}$) and $\Delta H_{HP2}$ (−25.8 kcal $mol^{-1}$) values for dmpm also correspond to the formation of $HP^\frown P^+$ and $HP^\frown PH^{2+}$, respectively.

For the titrations of dppb, dppent, and dpph, significant amounts of $P^\frown P$ and $HP^\frown PH^{2+}$ are likely to be present after the addition of 1 equiv of acid because $pK_{a1}$ and $pK_{a2}$ are probably very similar considering the $pK_a$ trend for the dppm, dppe, and dppp series of ligands (Table I). Thus, titrations of these ligands give $\Delta H_{HP1}$ values that correspond to the formation of a mixture of $P^\frown P$, $HP^\frown P^+$, and $HP^\frown PH^{2+}$. However, since the P donors in these ligands are separated so far, $\Delta H_{HP1}$ and $\Delta H_{HP2}$ are very similar anyway.

Previously[5] it was shown that there is a linear correlation (eq 6) between the $\Delta H_{HP}$ and $pK_a$ values of monodentate phosphines. As noted above and in Table I, $pK_{a1}$ and $pK_{a2}$ values for several bidentate phosphines have also been determined.[10] As for the

$$-\Delta H_{HP} = 16.3 + 1.82 pK_a; \quad \text{in kcal mol}^{-1} \tag{6}$$

monodentate phosphines, there is a correlation between $\Delta H_{HP1}$ and $pK_{a1}$ of bidentate phosphines. When plotted (Figure 2) on the same graph as the $\Delta H_{HP}$ and $pK_a$ values for monodentate phosphines, $\Delta H_{HP1}$ and $pK_{a1}$ values fall on the same line as that of the monodentate phosphines. A linear least-squares regression analysis of the data for both the mono- and bidentate ($\Delta H_{HP1}$) phosphines gives a new equation (eq 7) (correlation coefficient $r = 0.982$), which is only slightly different from that in eq 6.

$$-\Delta H_{HP} = 16.0 + 1.82 pK_a; \quad \text{in kcal mol}^{-1} \tag{7}$$

The $\Delta H_{HP2}$ values for dppm and dppe deviate (Figure 2) from eq 7. In these two diphosphines, the charges in the diprotonated species, $HP^\frown PH^{2+}$, are closest to each other and solvation may be different than in diprotonated phosphines in which the positive charges are separated by greater distances. For dppp and longer chain diphosphines, this separation of the $PPh_2H^+$ groups makes each end behave as independent phosphonium ions. The $pK_{a2}$ values for these longer chain bidentate phosphines, e.g., dppb, dppent, and dpph, can be calculated from eq 7. We also use eq 7 to predict $pK_{a1}$ values for other ligands in Table I for which $\Delta H_{HP1}$ values have been measured.

It is interesting to compare $\Delta H_{HP1}$ and $\Delta H_{HP2}$ data for the bidentate phosphines with $\Delta H_{HN1}$ and $\Delta H_{HN2}$ values for the

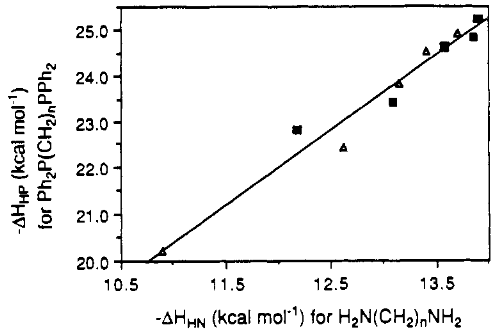

**Figure 3.** Plot of $\Delta H_{HP1}$ vs $\Delta H_{HN1}$ (■) and $\Delta H_{HP2}$ vs $\Delta H_{HN2}$ (▲) for $Ph_2P(CH_2)_nPPh_2$ and $H_2N(CH_2)_nNH_2$ ($n$ = 2–5). The $\Delta H_{HN1}$ and $\Delta H_{HN2}$ values are taken from ref 11a.

protonation of the diamines, $H_2N(CH_2)_nNH_2$ ($n$ = 2–6), with $HNO_3$ in water[11] (eqs 8 and 9). As for the $Ph_2P(CH_2)_nPPh_2$

$$N^\frown N + H^+ \xrightarrow[25.0\ ^\circ C]{H_2O} HN^\frown N^+ \tag{8}$$

$$HN^\frown N^+ + H^+ \xrightarrow[25.0\ ^\circ C]{H_2O} HN^\frown NH^{2+} \tag{9}$$

series, $-\Delta H_{HN1}$ increases with the number of $CH_2$ groups until it levels off at ~$n = 4$ (Figure 1). The relative effect of alkyl chain length on phosphorus basicity versus nitrogen basicity can be obtained by plotting $\Delta H_{HP1}$ vs $\Delta H_{HN1}$ and $\Delta H_{HP2}$ vs $\Delta H_{HN2}$ (Figure 3) for ligands with the same number ($n$) of $CH_2$ groups. When plotted on the same graph, one line correlating the $\Delta H_{HP1}$, $\Delta H_{HN1}$ and the $\Delta H_{HP2}$, $\Delta H_{HN2}$ data can be drawn (Figure 3). A linear least-squares analysis gives eq 10 ($r = 0.979$). The slope

$$-\Delta H_{HPx} = 2.64 + 1.61(\Delta H_{HNy}); \quad \text{in kcal mol}^{-1} \tag{10}$$
$$\text{for } x = 1, y = 1$$
$$\text{for } x = 2, y = 2$$

of 1.61 shows that the relative effect of the $PPh_2$ (or $PPh_2H^+$) groups on phosphorus basicity drops off more rapidly than the effect of $NH_2$ (or $NH_3^+$) on nitrogen basicity as the $(CH_2)_n$ link is lengthened. It is not clear why this is true but NH–hydrogen bonding to the water solvent is likely to be an important factor.

**$\Delta H_{HP1}$ and $\Delta H_{HP2}$ Values for Other Bidentate Phosphines.** The less exothermic $\Delta H_{HP1}$ value for dppbz (−21.3 kcal $mol^{-1}$) compared to dppe (−22.8 kcal $mol^{-1}$) demonstrates the electron-withdrawing character of the unsaturated chelate backbone[10] as compared with $-CH_2CH_2-$. The basicity of dppbz is more comparable to that of $PPh_3$ (−21.2 kcal $mol^{-1}$)[5] than to that of $PPh_2Me$ (−24.7 kcal $mol^{-1}$),[5] which suggests that the $PPh_2$ group in dppbz has the same electronic effect as the ortho H in $PPh_3$. Thus, while the $PPh_2$ group is electron-withdrawing[9] in the $Ph_2P(CH_2)_nPPh_2$ series of ligands, this is not the case in dppbz. That $PPh_2$ and H have similar electronic effects in aromatic systems is supported by the $\sigma_p$ value (−0.01)[12] for $PPh_2$ obtained from measurements of dissociation constants of substituted phosphinic and benzoic acids in aqueous THF. However, others[13] have suggested that the $PPh_2$ group is electron-withdrawing ($\sigma_p = 0.19$) in aromatic systems. Our results support the former conclusion.

The difference between $\Delta H_{HP1}$ and $\Delta H_{HP2}$ is much larger for dppbz (10.6 kcal $mol^{-1}$) than for dppe (2.6 kcal $mol^{-1}$). This suggests that the positive charge on the adjacent $PPh_2H^+$ group is more effectively transferred through the unsaturated 1,2-phenylene bridge in dppbz than through the $-CH_2CH_2-$ link in dppe. It is also possible that the rigid 1,2-phenylene bridge, which maintains the two $PPh_2H^+$ groups in the diprotonated dppbz

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species in close proximity, will also make $\Delta H_{HP2}$ less exothermic as compared with that in the more flexible dppe ligand. However, the latter factor probably does not contribute more than 1 or 2 kcal mol$^{-1}$ since *cis*- and *trans*-dppv, which also have unsaturated bridges, both also have similar large differences (9.9 and 9.0 kcal mol$^{-1}$, respectively) between $\Delta H_{HP1}$ and $\Delta H_{HP2}$.

As for dppbz, the *cis*- and *trans*-dppv ligands are also less basic than dppe (Table I). The $\Delta H_{HP1}$ measurements show *cis*-dppv to be 1.8 kcal mol$^{-1}$ less basic than *trans*-dppv; the same trend is observed in their p$K_{a1}$ values[10] (2.27 and 2.74, respectively). In addition, the heats of reaction ($\Delta H_{Hg}$)[14] of these compounds with Lewis acids $HgX_2$ (X = Cl, Br, I) (eq 11) follow the same

$$\widehat{P\;P} + HgX_2 \rightarrow \widehat{P\;P}HgX_2;\quad \Delta H_{Hg} \qquad (11)$$

trend with *cis*-dppv ($\Delta H_{Hg} = -80$ kcal mol$^{-1}$, X = Cl) being 7 kcal mol$^{-1}$ less basic toward these Lewis acids than *trans*-dppv ($\Delta H_{Hg} = -87$ kcal mol$^{-1}$, X = Cl). (*cis*- and *trans*-Dppv behave only as monodentate ligands toward $HgCl_2$.)[14] The greater $\Delta H_{HP1}$ basicity of the *trans*-dppv compound than *cis*-dppv may be due to better stabilization of the positive charge in the monoprotonated product by p–π conjugation of the lone pair of electrons on the unprotonated :$PPh_2$ group. As :$PPh_2$ is more free to rotate about the P–C(vinyl) bond in the trans isomer than in the more sterically congested cis isomer, the lone pair of electrons on phosphorus may better orient itself to allow conjugation with the π-orbitals of the vinyl group.

The $\Delta H_{HP2}$ values (−10.0 and −12.7 kcal mol$^{-1}$) for *cis*- and *trans*-dppv are substantially less negative than $\Delta H_{HP1}$ for these ligands. The p$K_{a2}$ values for *cis*- and *trans*-dppv could not be measured by the potentiometric method because their basicities were too low.[10] The successful determinations of the $\Delta H_{HP2}$ values for *cis*-dppv and *trans*-dppv demonstrate the usefulness of the calorimetric technique for measuring basicities of weakly basic compounds. The weak donor character of the second phosphorus in these compounds is also illustrated by the report that *cis*- and *trans*-dppv are known to form only 1:1 adducts with $HgX_2$ (eq 11),[14] even when 2 equiv of $HgX_2$ are used. As for dppbz, the weakly exothermic $\Delta H_{HP2}$ values for *cis*- and *trans*-dppv compared to that (−20.2 kcal mol$^{-1}$) of dppe indicates that the electron-withdrawing effect of the proton bound to one phosphorus atom is effectively transmitted through the unsaturated vinyl group in the dppv molecule to substantially lower the basicity of the second phosphorus atom. Electrostatic repulsion between the mutually *cis*-$PPh_2H^+$ groups in *cis*-dppv$H_2^{2+}$ could account in part for the even lower $\Delta H_{HP2}$ basicity of *cis*-dppv than *trans*-dppv.

The similarity of the basicity of *trans*-dppv to that of $PPh_3$ as determined by both $\Delta H_{HP}$ and p$K_a$ measurements (Table I) suggests that the *trans*-CH=CHPPh$_2$ and Ph groups have essentially the same effect on phosphorus basicity. This observation is supported[14] by $\Delta H_{Hg}$ values (eq 11) for Lewis adduct formation of $HgBr_2$ with *trans*-dppv (−79 ± 2 kcal mol$^{-1}$), $PPh_3$ (−77 ± 4 kcal mol$^{-1}$), and $PPh_2(CH{=}CH_2)$ (−78 ± 2 kcal mol$^{-1}$), which are the same within experimental error.

For the arphos ligand the $\Delta H_{HP1}$ value (−23.2 ± 0.4 kcal mol$^{-1}$) is comparable to $\Delta H_{HP1}$ of dppe (−22.8 ± 0.2 kcal mol$^{-1}$), which indicates that protonation occurs at the phosphorus atom, and $AsPh_2$ is, within experimental error, as electron withdrawing as $PPh_2$. The much lower $\Delta H_{HP2}$ value (−8.2 kcal mol$^{-1}$) of arphos, as compared with that (−20.2 kcal mol$^{-1}$) of dppe is consistent with protonation of the As atom in the second step. These protonation assignments are in accord with the lower basicity of $AsPh_3$ (p$K_B$ = 10.60) compared with $PPh_3$ (p$K_B$ = 8.57), as determined in anhydrous acetic acid.[15] It was, however, not possible to confirm the site of initial protonation by $^1$H NMR studies of arphos with $CF_3SO_3H$ in $CDCl_3$ because of rapid proton exchange.

The greater basicity of the phosphorus in arphos is also supported by calorimetric studies of its reaction with the Lewis acid $BH_3$.[16] The heat of adduct formation of $BH_3$(g) with the phosphorus in $Ph_2PCH_2CH_2AsPh_2$ is −155.3 kcal mol$^{-1}$, while that for the subsequent addition of $BH_3$ to the arsenic atom is −103.3 kcal mol$^{-1}$. These values are very similar to those for $BH_3$ addition to $PPh_3$ (−153.4 kcal mol$^{-1}$) and $AsPh_3$ (−111.3 kcal mol$^{-1}$).[16]

The $\Delta H_{HP1}$ value of dmpm (−31.0 kcal mol$^{-1}$) is notably similar to that of the very basic $PMe_3$ (−31.6 kcal mol$^{-1}$).[5] Thus, the $PMe_2$ group in dmpm may be considered about as electron donating as H and certainly more donating than a $PPh_2$ group in dppm. With use of the previously determined p$K_a$ value[10] for depe and eq 7, $\Delta H_{HP1}$ for depe is calculated to be −31.3 kcal mol$^{-1}$; thus, depe is slightly more basic than dmpm, which is consistent with the greater basicity of $PEt_3$ (−33.7 kcal mol$^{-1}$) as compared with that of $PMe_3$ (−31.6 kcal mol$^{-1}$).[5]

When the bidentate phosphine ligands in Table I are arranged according to their $\Delta H_{HP1}$ values, their basicities decrease in the following order:

depe ≥ dmpm ≫ dpph > dppent > dppb > dppp > dppe >
dppm > *trans*-dppv > dppbz > *cis*-dppv

The same trend is also observed in the $\Delta H_{HP2}$ values. Since this series summarizes the energetics of phosphine bond formation with $H^+$, it presumably also represents the relative σ-donating abilities of bidentate phosphines toward metals in their metal complexes. This property appears otherwise difficult to obtain as calorimetric studies of silver(I)[17] and $HgX_2$ (X = Cl, Br, I)[14] with dppm, dppe, and dppp give a complicated array of products where the bidentate phosphines behave as chelate,[14,17] bridging,[17] and/or monodentate[14] ligands.

We have also determined the $\Delta H_{HP}$ of the monodentate $(p\text{-}CF_3C_6H_4)_3P$, which is presumed to be very weakly basic.[2a] The $\Delta H_{HP}$ value of −13.6 kcal mol$^{-1}$ corresponds to a p$K_a$ value of −1.32 by application of eq 7. Thus, in the isosteric series (i.e., cone angle = 145°) $(p\text{-}XC_6H_4)_3P$ (X = $CF_3$, Cl, F, H, Me, OMe, $NMe_2$),[2a] the trifluoromethyl-substituted compound is by far the weakest base.

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