$\epsilon = 4.0r$ (distance-dependent dielectric). The rms deviation in $\omega$ from planarity agreed best with the crystal for weak electrostatic potentials ($\epsilon = 4.0$ and $4.0r$). Similar results were found by Vedani and Dunitz.[32] The best results used a 6.0-Å residue-based nonbonding cutoff with a distance-dependent dielectric constant of $4.0r$. Similar results could be obtained with a 9.0-Å atom-based nonbonding cutoff. We found that the results with explicit solvent or large portions of the crystal environment did not justify the extra computational time needed to run them.

Thus, empirically the best overall condition for minimization with AMBER are Jorgensen's "united atom" VDW, $\epsilon = 4.0r$, and 6.0-Å residue-based or a 9.0-Å atom-based nonbonding cutoff. A dielectric constant ($\epsilon$) of $4.0r$ is a weak electrostatic potential. These appear to be necessary in minimizations in order to correct for the omissions of solvent and of atomic motion (i.e., to model the room temperature structure). Inclusion of solvent explicitly results in better agreement for the surface of the protein but does not remove the need for a weaker electrostatic potential. Our results suggest that further improvements in potential functions are still needed to model high resolution structures and to ultimately predict protein structure accurately.

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# The Structures and Energetics of Fluorine-Substituted Phosphonium Ylides

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**Abstract:** The electronic structures and energies of the model ylides $H_3PCXY$ and their isomeric phosphines $H_2PCHXY$ (X = Y = H, F, $CF_3$ and X = H, Y = F) have been determined from ab initio molecular orbital theory at the SCF level. The calculations were performed with a double-$\zeta$ basis set augmented by polarization (d) functions on both the P atom and the C atom bonded to P and a set of diffuse s and p functions on the C atom bonded to P. The $H_3PCH_2$, $H_3PCHF$, and $H_3PC(CF_3)_2$ ylides exhibit varying degrees of P–C multiple bonding and zwitterionic character. The ylidic carbon in $H_3PCHF$ is more pyramidal than that in $H_3PCH_2$, but it is planar in $H_3PC(CF_3)_2$. The structure of $H_3PCF_2$ is entirely different, and it closely resembles the isolated $H_3P$ and $:CF_2(^1A_1)$ species separated by 3.54 Å. The energies for ylide to phosphine isomerizations were calculated to assess ylide stabilities and to derive ylide heats of formation. From the calculated energies of ylide to lowest singlet state carbene dissociations, the $H_3PCH_2$, $H_3PCHF$, $H_3PC(CF_3)_2$, and $H_3PCF_2$ binding energies were found to be 53.2, 16.6, 77.3, and 1.2 kcal/mol, respectively. The theoretical properties of the fluorinated ylides are compared to available experimental data and known solution chemistry.

Several recent studies[1-5] have used molecular orbital theory to characterize the structure and energetics of ylides, which are important synthetic intermediates.[6] These studies focussed on simple model structures of the form $H_3X^+CH_2^-$ (X = N, P) and $H_2X^+CH_2^-$ (X = O, S) where the substituent on carbon is always hydrogen. The model ylide $H_3P^+CH_2^-$ has been studied in detail and is expected to have partial double bond character in the P–C bond. The calculated value for $r$(P–C) is in reasonable agreement with that observed in X-ray structure determinations of substituted ylides.[7-10]

Fluorinated phosphonium ylides also have proved to be useful intermediates in synthesis,[11-13] but their properties vary dramatically depending upon whether fluorine is substituted $\alpha$ or $\beta$ to the ylidic carbon. Ylides that have no $\alpha$-fluorines ordinarily are isolable. For example, $(C_2H_5O)_3PC(CF_3)_2$,[14] $Ph_3PC(CF_3)_2$,[15] and $Ph_3PC(CF_3)C_2F_5$[16] have been made and fully characterized, and the crystal structure of **1** has been determined.[16,17] By

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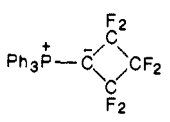
**Table I.** Bond Distances and Angles for Phosphines and the Isomeric Ylides[a]

| | | | |
|---|---|---|---|
| | $H_2PCH_3$[b] | | |
| r(P–C) | 1.856 (1.863) | θ(PCH) | 112.7 (109.2) |
| r(C–H) | 1.082 (1.093) | θ(PCH′) | 109.6 (109.2) |
| r(C–H′) | 1.083 (1.093) | θ(HCH) | 108.6 (109.6) |
| r(P–H) | 1.404 (1.414) | θ(HCH′) | 107.6 (109.6) |
| | | θ(CPH) | 97.8 (97.5) |
| | | θ(HPH) | 94.7 (93.4) |
| | $H_2PCH_2F$ | | |
| r(P–C) | 1.854 | θ(PCH) | 110.0 |
| r(C–H) | 1.082 | θ(PCF) | 113.3 |
| r(C–F) | 1.383 | θ(HCF) | 107.4 |
| r(P–H) | 1.401 | θ(HCH) | 108.8 |
| | | θ(CPH) | 97.6 |
| | | θ(HPH) | 95.6 |
| | $H_2PCHF_2$ | | |
| r(P–C) | 1.873 | θ(PCH) | 115.4 |
| r(C–H) | 1.078 | θ(PCF) | 109.5 |
| r(C–F) | 1.353 | θ(FCH) | 107.5 |
| r(P–H) | 1.403 | θ(FCF) | 106.9 |
| | | θ(CPH) | 95.1 |
| | | θ(HPH) | 94.5 |
| | $H_2PCH(CF_3)_2$ | | |
| r(P–C) | 1.917 | θ(PCC′) | 110.2 |
| r(C–C) | 1.518 | θ(PCH) | 111.0 |
| r(C–H) | 1.085 | θ(C′CH) | 106.3 |
| r(P–H) | 1.396 | θ(C′CC′) | 112.7 |
| r(C′–F) | 1.375 | θ(CPH) | 95.0 |
| r(C′–F′) | 1.366 | θ(HPH) | 94.9 |
| r(C′–F″) | 1.368 | θ(CC′F) | 108.8 |
| | | θ(CC′F′) | 114.2 |
| | | θ(CC′F″) | 113.3 |
| | | θ(FC′F′) | 106.4 |
| | | θ(FC′F″) | 106.8 |
| | | θ(F′C′F″) | 106.9 |

| | | | |
|---|---|---|---|
| | $H_3PCH_2$[c] | | |
| r(P–C) | 1.675 (1.668) | θ(PCH) | 118.4 (119.2) |
| r(C–H) | 1.076 (1.075) | θ(HCH) | 117.4 (120.4) |
| r(P–H) | 1.414 (1.401) | θ(CPH) | 127.7 (118.6) |
| r(P–H′) | 1.389 (1.401) | θ(CPH′) | 112.1 (117.7) |
| | | θ(HPH′) | 98.5 (99.7) |
| | | θ(H′PH′) | 105.1 (99.9) |
| | $H_3PCHF$ | | |
| r(P–C) | 1.723 | θ(PCH) | 115.8 |
| r(C–H) | 1.079 | θ(PCF) | 113.0 |
| r(C–F) | 1.395 | θ(FCH) | 109.7 |
| r(P–H) | 1.414 | θ(PCH) | 131.7 |
| r(P–H′) | 1.384 | θ(PCH′) | 109.6 |
| r(P–H″) | 1.384 | θ(PCH″) | 106.4 |
| | | θ(HPH′) | 99.6 |
| | | θ(HPH″) | 100.5 |
| | | θ(H′PH″) | 106.9 |
| | $H_3PCF_2$ | | |
| r(P–C) | 3.54 | θ(PCF) | 104.2 |
| r(C–F) | 1.288 | θ(FCF) | 104.8 |
| r(P–H) | 1.403 | θ(CPH) | 165.1 |
| r(P–H′) | 1.401 | θ(CPH′) | 94.1 |
| | | θ(HPH′) | 95.9 |
| | | θ(H′PH′) | 95.2 |
| | $H_3PC(CF_3)_2$ | | |
| r(P–C) | 1.707 | θ(PCC′) | 120.8 |
| r(C–C′) | 1.469 | θ(C′CC′) | 118.2 |
| r(P–H) | 1.392 | θ(CPH) | 118.9 |
| r(P–H′) | 1.381 | θ(CPH′) | 112.4 |
| r(C–F) | 1.389 | θ(HPH′) | 103.3 |
| r(C–F′) | 1.382 | θ(H′PH′) | 105.3 |
| r(C–F″) | 1.379 | θ(CC′F) | 110.0 |
| | | θ(CC′F′) | 115.5 |
| | | θ(CC′F″) | 114.6 |
| | | θ(FC′F′) | 105.5 |
| | | θ(FC′F″) | 106.1 |
| | | θ(F′C′F″) | 104.4 |

[a] Bond distances in Å. Bond angles in deg. [b] Experimental values in parentheses from ref 28. [c] Parabollically optimized values in parentheses from ref 1.

contrast, the fluoromethylene ylides $R_3PCHF$ and $R_3PCF_2$ are unstable. The former can be pregenerated in solution at low temperatures, but it has no appreciable lifetime at 28 °C.[13] The latter, however, cannot be pregenerated, and its existence can only be inferred from its reactions.[11,18] In fact, there is cogent evidence that $R_3PCF_2$ species (R = Ph, $Me_2N$, EtO) readily dissociate into $R_3P$ and $:CF_2$.[19,20]



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To date there is only qualitative information on fluorinated phosphonium ylide stability, and there are no experimental data on the structures of α-fluorinated phosphonium ylides. In this paper we present the results of ab initio calculations of the structures and energetics of the model ylides $H_3PCXY$ and their isomeric phosphines $H_2PCHXY$ with X = Y = H, F, $CF_3$ and X = H, Y = F. The energetics of ylide to phosphine isomerizations and ylide to carbene dissociations are computed to assess the effects of fluorination on ylide stability. The bonding in the ylides, based on their computed structures and electronic properties (atomic and group charges, dipole moments, and HOMO energies), is discussed and is related to the ylide stabilities.

## Calculations

All calculations were done at the SCF level with the program HONDO[24] on an IBM 3081 computer. The geometries were determined by complete gradient optimization[25] in the conformations and symmetries given in Figure 1. The calculations were done with the following basis set following our previous work on ylides[1] and carbenes.[26] The starting basis set is of double-ζ quality with coefficients and exponents for the s and p functions from Dunning and Hay.[27] The phosphorus and ylidic carbon basis sets are augmented by a set of d polarization functions with exponents of $\zeta_d(C) = 0.75$ and $\zeta_d(P) = 0.50$. Because the formal valence bond structure for the ylide places a negative charge on carbon ($H_3P^+C^-XY$), we have augmented the carbon basis set with a set of diffuse s and p functions with exponents $\zeta_s(C) = 0.04548$ and $\zeta_p(C) = 0.034$.[1] The basis set thus has the following form: P, (11,7,1)/[6,4,1]; ylidic C, (10,6,1)/[4,3,1]; substituent C and F, (9,5)/[3,2]; and H, (4)/[2].

## Results and Discussion

**Geometries.** The calculated geometry parameters are given in Table I with reference to the labeling in Figure 1. We first discuss

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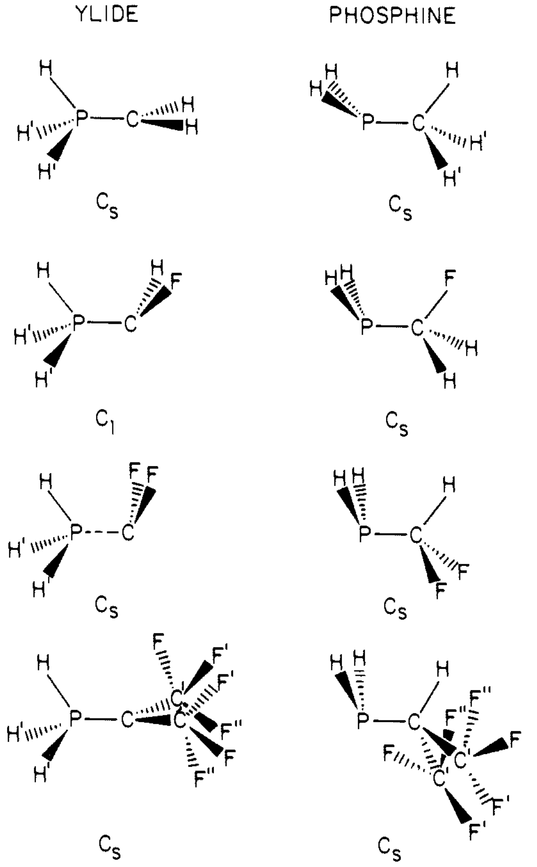
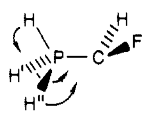


**Figure 1.** Line drawings of fluorinated ylides and their isomeric phosphines showing the molecular symmetries and atomic labels.

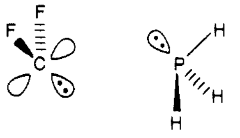
the structure of the non-zwitterionic isomers, the substituted phosphines. The structure of $CH_3PH_2$ is known from experiment[28] and, as seen in Table I, the agreement with experiment is excellent. The structures of the other phosphines are not known from experiment, although that for $P(CF_3)_3$ has been determined.[29] As one fluorine is substituted for hydrogen to form $H_2PCH_2F$, there is essentially no change in $r$(P–C). Substitution of a second F leads to an increase in $r$(P–C) of 0.017 Å. This is consistent with the experimental observation that $r$(P–C) increases in going from $P(CH_3)_3$ to $P(CF_3)_3$. As expected,[30] the C–F bond lengths decrease with an increase in fluorine substitution. The geometric parameters at P show little change on substitution of F at C except that $\theta$(CPH) decreases by 2° in going from $H_2PCH_3$ to $H_2PCHF_2$. Substitution of two $CF_3$ groups for H in $H_2PCH_3$ leads to an increase in the P–C bond of 0.061 Å, which is very similar to the increase of 0.058 Å found in going from $P(CH_3)_3$ to $P(CF_3)_3$.[29] Other than this change, there are no other major differences in the geometric parameters common to $H_2PCH_3$ and $H_2PCH(CF_3)_2$. The C–F bonds in $H_2PCH(CF_3)_2$ are too long at this level of calculation since there are no polarization functions on the carbon in this group[31] and the distances should not be compared to $r$(C–F) found for $H_2PCH_2F$ or $H_2PCHF_2$.

The difference between the structures of the phosphonium ylides and their phosphine isomers varies markedly with the degree of fluorine substitution. We first compare our more accurate gradient optimized structure for $H_3PCH_2$ with that previously optimized parabollically using the same basis set.[1] Although the basic structure remains the same, there are some changes in the parameters. The largest changes are found for the unique P–H bond where $\theta$(CPH) increases by 9° and $r$(P–H) decreases by 0.013 Å as compared to the parabollic optimized structure. The other P–H bonds shorten by 0.01 Å. The gradient optimized structure has a P–C bond that is 0.013 Å longer and the $CH_2$ group is slightly more pyramidal ($\sum\theta_i = 354.2°$), although this still should certainly not be described as a pyramidal carbon. The gradient optimized value for $r$(P–C) in the ylide is 0.181 Å smaller than that in $H_2PCH_3$, which indicates significant multiple-bond character in $H_3PCH_2$.

Substitution of one fluorine for hydrogen leads to some changes in the structure of the ylide. The P–C bond lengthens to 1.723 Å and thus the decrease in $r$(P–C) going from $H_2PCH_2F$ to $H_3PCHF$ is only 0.131 Å. However, this decrease is still significant and reflects some multiple-bond character in the ylide bond, albeit less than that in $H_3PCH_2$. Notably, the carbon is more pyramidal in $H_3PCHF$ ($\sum\theta_i = 338.5°$), in accord with the increase in $r$(P–C). In comparison with $H_2PCH_2F$, the C–F bond is 0.012 Å longer in the ylide and indicates increased negative charge at the carbon.[32] The $\theta$(CPH) bond angle increased by 4° in $H_3PCHF$ and, consequently, the $\theta$(CPH′) and $\theta$(CPH″) bond angles decrease from the value for $\theta$(CPH′) in $H_3PCH_2$. Thus, the unique gauche H in the $PH_3$ group rocks away from the CHF group. Neither the internal HPH bond angles nor the P–H bond lengths show large changes on substitution of one fluorine at carbon.



Substitution of a second fluorine to form $H_3PCF_2$ leads to a dramatic change in structure, namely, dissociation into weakly interacting $PH_3$ and $:CF_2(^1A_1)$ fragments. The ylide closely resembles the isolated species separated by 3.54 Å. The geometry of $PH_3$ itself at this level of calculation has $r$(P–H) = 1.403 Å and $\theta$(HPH) = 95.1°,[33] which are essentially the same values in $H_3PCF_2$. The geometry of $:CF_2(^1A_1)$, optimized with a different double-$\zeta$ basis set and a two-configuration wave function,[34] gave values of 1.305 Å and 104.3° for $r$(C–F) and $\theta$(FCF), respectively, which compare to our values of 1.288 Å and 104.8° in $H_3PCF_2$. The agreement in angle is excellent, and the small difference in C–F bond length can be attributed largely to differences in the basis sets and forms of the wave function. The orientation of the $CF_2$ group with respect to $PH_3$ is shown below and the lone pairs are found to approximately parallel ($\theta$(PCF) = 104.2°).



To compare our optimized structure for $H_3PCF_2$ with one that much more closely resembles a typical ylide, we computed the total energy for $H_3PCF_2$ fixed at the geometry found for $H_3PCHF$ (F was substituted for H in $H_3PCHF$ and the C–F bonds were set at 1.395 Å). This structure was 25 kcal/mol higher in energy than the dissociated species.

Although the dissociated nature of the ylide is similar to that found for $H_2OCH_2$,[1] the details of the structure are quite different. The oxonium ylide resembles a $:CH_2(^1A_1)$ carbene solvated by water, but the lone pairs are close to being perpendicular rather

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[33] Experimental values for $PH_3$: $r$(P–H) = 1.421 Å, $\theta$(HPH) = 93.8°. See: Burrus, C. A., Jr.; Jache, A.; Gordy, W. *Phys. Rev.* **1954**, *95*, 700.

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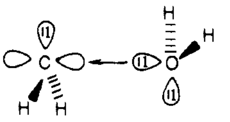
than parallel as in $H_3PCF_2$. Moreover, the C–O bond distance is 1.870 Å, which indicates a much stronger interaction than that found in $H_3PCF_2$.



Substitution of two $CF_3$ groups for H leads to a structure that is very similar to that of $H_3PCH_2$. The P–C bond length is 0.032 Å longer in $H_3PC(CF_3)_2$, but more important, it is 0.210 Å shorter than the P–C bond in $H_2PCH(CF_3)_2$. This is the largest decrease found between a phosphine and its isomeric ylide. The ylidic carbon in $H_3PC(CF_3)_2$ is planar. As a consequence the value for $\theta$(CPH) decreased by 9° from its value in $H_3PCH_2$, and $\theta$(CPH′) increased by ~5°. The C–C′ bonds are shorter by ca. 0.05 Å and the C′–F bonds are longer by ca. 0.015 Å in the ylide vs. the phosphine. These changes can be ascribed to anionic F hyperconjugation due to the anionic nature of the ylide carbon (vide infra).

Our optimized $H_3PC(CF_3)_2$ structure can be compared to the one available crystal structure of a fluorinated phosphonium ylide (**1**). Obviously, the comparison is inexact because the four-membered ring and the phenyl groups impose significant constraints on the structure of **1**. Nonetheless, our value for $r$(P–C) of 1.707 Å agrees very well with the crystal structure value of 1.713 Å, and the ylidic carbons are planar in both $H_3PC(CF_3)_2$ and **1**.

**Energetics.** We have shown previously that the $\Delta E$ for the isomerization reaction 1, which corresponds to an internal proton transfer from the non-zwitterionic isomer to the ylide, is a useful means to characterize the energetics of ylides.[1] Reaction 2 represents the dissociation of substituted phosphine to $PH_3$ and lowest singlet-state carbene. ($\Delta E$(rxn 2) − $\Delta E$(rxn 1) is equivalent to $\Delta E$ for dissociation of ylide into $PH_3$ and singlet carbene). The total energies and singlet–triplet splittings for $:CH_2$, $:CF_2$, $:CHF$, and $:C(CF_3)_2$ are available from earlier work.[26]

$$H_2PCHXY \rightarrow H_3PCXY \qquad (1)$$

$$H_2PCHXY \rightarrow H_3P + :CXY(^1A_1) \qquad (2)$$

If $\Delta E$ for reaction 1 is significantly less than that for reaction 2 then the ylide will be bound and should exhibit ylidic behavior. If $\Delta E$ for reaction 1 is greater than or equal to that of reaction 2, then the ylide will dissociate and should exhibit carbene behavior. From $\Delta E$ for reaction 1, which can be calculated directly from our total energies (Table II), the $\Delta H_f°$'s of the gas-phase ylides can be estimated, provided that $\Delta H_f°$'s for the substituted phosphines are available. The $\Delta E$ for the non-isodesmic reaction 2, however, cannot be reliably calculated from total energies at this theoretical level. The appropriate $\Delta H_f°$'s are required. Thus, the $\Delta H_f°$'s of the substituted phosphines are needed not only to calculate the $\Delta H_f°$'s of the ylides but also to calculate $\Delta E$ for reaction 2.

We first discuss our determinations of the required $\Delta H_f°$'s. The only reported $\Delta H_f°$'s for the phosphines of interest are an experimental value of 1.3 kcal/mol[35] for $PH_3$ and an estimated value of −7 kcal/mol for $H_2PCH_3$.[36] We can calculated $\Delta H_f°$'s for the phosphines from reactions 3–8 ($\Delta E_{calcd}$ in kcal/mol).[37,38]

| | $\Delta E_{calcd}$ | |
|---|---|---|
| $H_2PCH_3 + CH_4 \rightarrow PH_3 + C_2H_6$ | 3.9 | (3) |
| $H_2PCH_3 + CH_3F \rightarrow H_2PCH_2F + CH_4$ | −0.5 | (4) |
| $H_2PCH_2F + CH_4 \rightarrow PH_3 + CFH_2CH_3$ | −1.3 | (5) |
| $H_2PCH_3 + CH_2F_2 \rightarrow H_2PCHF_2 + CH_4$ | 2.4 | (6) |
| $H_2PCHF_2 + CH_4 \rightarrow PH_3 + CF_2HCH_3$ | −4.4 | (7) |
| $H_2PCH_3 + H_2C(CF_3)_2 \rightarrow H_2PCH(CF_3)_2 + CH_4$ | 5.4 | (8) |

Table II. Total Energies and Heats of Formation (Calculated and Experimental)[a]

| molecule | $E_{tot}$ (au) | ref | $\Delta H°_f$ (kcal/mol) | ref |
|---|---|---|---|---|
| $PH_2CH_3$ | −381.491 758[b] | c | −4.9 | c |
| $PH_2CH_2F$ | −480.355 755 | c | −43.6 | c |
| $PH_2CHF_2$ | −579.230 466 | c | −94.0 | c |
| $PH_2CH(CF_3)_2$ | −1 052.659 680[d] | c | −322.2 | c |
| $PH_3CH_2$ | −381.402 462[e] | c | 51.1 | c |
| $PH_3CHF$ | −480.248 520 | c | 23.7 | c |
| $PH_3CF_2$ | −579.150 685 | c | −43.9 | c |
| $PH_3C(CF_3)_2$ | −1 052.605 553[d] | c | −288.2 | c |
| $PH_3$ | −342.447 272 | c | 1.3 ± 0.4 | 35 |
| $CH_4$ | −40.200 951 | 31c | −17.8 ± 0.1 | 40 |
| $CH_3F$ | −139.064 168 | 31c | −56.8 ± 2 | 40 |
| $CH_2F_2$ | −237.943 547 | 31c | −108.1 ± 0.2 | 40 |
| $CH_3CH_3$ | −79.239 228 | 31c | −20.1 ± 0.0 | 40 |
| $CFH_2CH_3$ | −178.111 484 | 31c | −62.9 ± 0.4 | 40 |
| $CF_2HCH_3$ | −276.995 760 | 31c | −118.8 ± 2.0 | 40 |
| $CH_2(CF_3)_2$ | −711.377 404[d] | c | −340.5[f] | c |
| $CF_2(CF_3)_2$ | −909.262 367 | 31c | −426.2 ± 1.7 | 40 |
| $:CH_2$ | −38.902 014 | 26 | 103 | 41 |
| $:CHF$ | −137.800 438 | 26 | 39 | 41 |
| $:CF_2$ | −236.719 453 | 26 | −44 | 41 |
| $:C(CF_3)_2$ | −710.058 720[d,g] | 26 | −212.2[h] | c |
| $CH_2{=}CH_2$ | −78.042 712 | 31b | 12.5 ± 0.3 | 40 |
| $CH_2{=}CHF$ | −176.912 823 | 31b | −33.2 ± 0.4 | 40 |
| $CH_2{=}CF_2$ | −275.785 037 | 31b | −80.0 ± 0.8 | 40 |

[a] All total energies with DZ+$D_C$ or DZ+$D_{C,P}$ basis sets unless noted otherwise. Diffuse functions on C bound to P in each ylide and substituted phosphine. [b] $E_{tot}$ = −381.491 327 au without diffuse functions; $E_{tot}$ = −381.492 567 au with diffuse functions on both C and P. [c] This work. [d] DZ+$D_C$ on central carbon. No d functions on $CF_3$ carbons. [e] $E_{tot}$ = −381.402 901 au with diffuse functions on both C and P. [f] Estimated from group values, see ref 39. [g] $E$(DZ+$D_C$) = −710.234 454 au. [h] ±5 kcal/mol, see text.

The total energies required to determine $\Delta E$ are given in Table II. The use of known $\Delta H_f°$'s (see Table II) then allows us to calculate unknown $\Delta H_f°$'s, assuming $\Delta E_{rxn} \cong \Delta H°_{rxn}$. The value for $\Delta H_f°(H_2PCH_3)$ is −4.9 kcal/mol from reaction 3, which agrees reasonably well with the estimated value. For consistency, we have used our theoretical $\Delta H_f°(H_2PCH_3)$ value in all thermomechanical calculations. From reactions 4 and 5 the estimated values of $\Delta H_f°(H_2PCH_2F)$ are −44.4 and −42.5 kcal/mol, respectively. Considering the experimental uncertainity in the $\Delta H_f°(CH_3F)$ and $\Delta H_f°(H_2PCH_3)$ data, the agreement is very good and we average the values to get $\Delta H_f°(H_2PCH_2F)$ = −43.6 kcal/mol. The values for $\Delta H_f°(H_2PCHF_2)$ obtained similarly from reactions 6 and 7 are −92.7 and −95.3 kcal/mol, respectively. Again the agreement is good and we average to obtain $\Delta H_f°(H_2PCHF_2)$ = −94.0 kcal/mol. To obtain $\Delta H_f°(H_2PCH(CF_3)_2)$ we need $\Delta H_f°(CH_2(CF_3)_2)$, which is not known experimentally but can be reliably estimated to be −340.5 kcal/mol.[39] Thus, $\Delta H_f°(H_2PCH(CF_3)_2)$ = −322.2 kcal/mol.

To evaluate the energetics for reaction 2 we also require $\Delta H_f°$ of the carbenes in their lowest singlet states. The value for

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(35) Wagman, D. D.; Evans, W. H.; Parker, V. P.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data, Suppl. No. 2* **1982**, *11*.

(36) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

(37) The basis sets used to calculate $E_{tot}$ of reactants and products in equations 3–8 are not strictly consistent because diffuse functions were included only with the substituted phosphines, but this inconsistency does not significantly affect the results. For example, $\Delta E$ = 3.6 kcal/mol for reaction 3 with no diffuse functions in the basis set for $H_2PCH_3$. Diffuse functions on carbon in $H_2PCH_3$ do not affect the charges, HOMO eigenvalue, or dipole to any extent.

(38) We are making the approximation that $\Delta E \simeq \Delta H°$, which ignores corrections for differences in zero-point energies ($\Delta$ZPE). This should be a reasonable approximation for these systems. Any errors introduced should be smaller than the uncertainties in the experimental and estimated $\Delta H_f°$'s. For example, the $\Delta$ZPE corrections for eq 3 and 4 are −0.6 kcal/mol, and that for eq 5 is −0.8 kcal/mol.

(39) $\Delta H_f°(CH_2(CF_3)_2)$ was derived by group additivity using $\Delta H_f°$(C–(F)$_3$(C)) = −167.8 kcal/mol from Dolbier et al. (Dolbier, W. R., Jr.; Medinger, K. S.; Greenberg, A.; Liebman, J. F. *Tetrahedron*, **1982**, *38*, 2415) and $\Delta H_f°$(C–(H)$_2$(C)$_2$) = −4.9 kcal/mol from Benson (Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976).

(40) Pedley, J. B.; Rylance, J. *Sussex-N.P.L. Computer Analyzed Thermochemical Data: Organic and Organometallic Compounds*; University of Sussex: Sussex, Brighton, 1977.

**Table III.** Energetics for Reactions 1 and 2 (kcal/mol)

| X | Y | $\Delta E$(rxn. 1)[a] | $\Delta E$(rxn. 2)[b,c] | $\Delta E$(rxn. 2)[d] |
|---|---|---|---|---|
| H | H | 56.0 | 109.2 | 99.2 |
| H | F | 67.3 | 83.9 | 92.0 |
| F | F | 50.1 | 51.3 | 97.3 |
| $CF_3$ | $CF_3$ | 34.0 | 111.3 | 93.5 |

[a] $\Delta E = E(H_3PCXY) - E(H_2PCHXY)$. Total energies from Table II. [b] $\Delta E \simeq \Delta H_f°(PH_3) + \Delta H_f°(:CXY) - \Delta H_f°(H_2PCHXY)$. Heats of formation from Table II. [c] Singlet carbenes. [d] Triplet carbenes. Evaluated by adding the singlet-triplet splitting from ref 26 to $\Delta E$ in the second column. For $:CH_2$, the correction is from experiment; see ref 26 and 41.

$\Delta H_f°(:CH_2)(^1A_1)$ is known experimentally to be 103 kcal/mol.[41] Experimental values for $\Delta H_f°(:CHF)(^1A_1)$ range from 26 to 39 kcal/mol.[41] We prefer the higher value for reasons discussed below. The experimental value for $\Delta H_f°(:CF_2)(^1A_1)$ is known more precisely, and we use the value of −44 kcal/mol, although it may be as low as −49 kcal/mol.[41] Since $\Delta H_f°(:C(CF_3)_2)$ is not known, we must estimate its value. It can be derived from isodesmic reactions 9 and 10.

$$:C(CF_3)_2(^1A_1) + CH_4 \rightarrow CH_2(CF_3)_2 + :CH_2(^1A_1) \quad (9)$$

$$:C(CF_3)_2(^1A_1) + CH_2F_2 \rightarrow CH_2(CF_3)_2 + :CF_2(^1A_1) \quad (10)$$

The direct calculation of $\Delta H_f°(:C(CF_3)_2)$ from reaction 9 gives −207.3 kcal/mol,[42] whereas reaction 10 gives −217.0 kcal/mol. Since this discrepancy is larger than what we normally find for calculations on isodesmic reactions, the average value of −212.2 kcal/mol that is reported in Table II should be considered as only a rough estimate. (An error of even twice 5 kcal/mol, however, would not alter our findings that follow).

The energetics for reactions 1 and 2 are given in Table III.[43] Comparison of the energetics for (1) and (2) shows that the ylides with X = Y = H and X = Y = $CF_3$ are very strongly bound with respect to dissociation to the phosphine and singlet carbene and are "stable" in this sense.[44] By contrast, the ylide with X = Y = F is bound by only 1.2 kcal/mol with $\Delta H_f°(:CF_2) = -44$ kcal/mol and would be unbound by 3.8 kcal/mol if $\Delta H_f°(:CF_2) = -49$ kcal/mol. The low binding energy of $H_3PCF_2$ is consistent with its dissociated structure[45] and the observed fragmentation of its derivatives in solution.[19]

The large uncertainty in the experimental value of $\Delta H_f°(:CHF)$ leaves some doubt about the results for X = H, Y = F. The $\Delta E$ for reaction 2 cited in Table III is based on $\Delta H_f°(:CHF) = 39$ kcal/mol and indicates $H_3PCHF$ is bound by 16.6 kcal/mol. If, however, the lower $\Delta H_f°$ value of 26 kcal/mol is used, the ylide is bound by only 3.5 kcal/mol, which is about the same binding energy for $H_3PCF_2$. This does not seem reasonable on the basis of the markedly different structures of the ylides and the significant multiple bonding associated with the P–C bond in $H_3PCHF$. Further evidence for the higher $\Delta H_f°$ value for :CHF comes from $\Delta E$ for isodesmic reaction 11. At the DZ+D$_C$ level with two configuration wave functions, $\Delta E$ = 12.8 kcal/mol and thus $\Delta H_f°(:CHF) \simeq 35.9$ kcal/mol, using the experimental $\Delta H_f°$ values for $:CH_2$ and $:CF_2$ in Table II.

$$:CF_2(^1A_1) + :CH_2(^1A_1) \rightarrow 2\ :CHF(^1A_1) \quad (11)$$

The heats of formation of the ylides derived from Reaction 1 are given in Table II. A check on $\Delta H_f°(H_3PCHF)$ and $\Delta H$-$(H_3PCF_2)$ and thus an independent check on $\Delta E$ for reaction 1 can be made by calculating with our basis set the energies (in kcal/mol) for isodesmic reactions 12 and 13. Using our calculated value for $\Delta H_f°(H_3PCH_2)$ we find $\Delta H_f°(H_3PCHF)$ = 20.5 kcal/mol and $\Delta H_f°(H_3PCF_2)$ = −44.8 kcal/mol in excellent agreement with the respective values of 23.7 kcal/mol and −43.9 kcal/mol derived from reaction 1.

| | $\Delta E_{calcd}$ | |
|---|---|---|
| $H_3PCH_2 + CH_2{=}CHF \rightarrow H_3PCHF + CH_2{=}CH_2$ | 15.1 | (12) |
| $H_3PCH_2 + CH_2{=}CF_2 \rightarrow H_3PCF_2 + CH_2{=}CH_2$ | −3.7 | (13) |

An important factor contributing to the stabilization of the ylides is the ability of the carbanionic carbon to the planar. It is well established that carbanions with $\alpha$-fluorines are pyramidal, e.g., the barrier to inversion for $CF_3^-$ is 119 kcal/mol.[46] Thus in $H_3PCF_2$ there is a strong driving force to make the carbon pyramidal and the lone pair therefore is not able to form a multiple bond with the phosphorus and stabilize the ylide. Since the $:CF_2$ singlet carbene is so relatively stable, there is a low energy dissociation path and a stable ylide will not form. For $H_3PCHF$, the carbon still wants to be pyramidal but the driving force is not as strong. (The inversion barrier in $CH_2F^-$ is about 17 kcal/mol.)[47] Consequently, the carbon can form a partial multiple bond with phosphorus, but the bond is not as strong as those formed in $H_3PCH_2$ or $H_3PC(CF_3)_2$ as evidenced by the greater $\Delta E$ for reaction 1 and the relatively longer P–C bond in $H_3PCHF$. The inversion barrier in $CH_3^-$ is very low (<2 kcal/mol),[48] and thus the carbon in $H_3PCH_2$ is essentially planar and can form a strong multiple bond with the phosphorus. This effect is even more pronounced in $H_3PC(CF_3)_2$ which has $\beta$-fluorines to stabilize a planar carbanion by hyperconjugation. The $\Delta E$ of −16.7 kcal/mol for reaction 14 reveals the stabilizing effect of the two $CF_3$ groups, whereas the $\Delta E$ of 10.8 kcal/mol for reaction 15 shows that the F substituent is destabilizing.

$$H_3PCH_2 + CH_2(CF_3)_2 \rightarrow H_3PC(CF_3)_2 + CH_4 \quad (14)$$

$$H_3PCH_2 + CH_3F \rightarrow H_3PCHF + CH_4 \quad (15)$$

**Electronic Properties.** Several electronic properties of the phosphines and ylides are summarized in Table IV. The analyses of these properties are in line with our earlier discussions of ylide structure and bonding. Again it is appropriate to compare the ylide with its isomeric phosphine to look for changes. Comparison of $H_3PCH_2$ with $H_2PCH_3$ reveals that four major changes occur on isomerization: (1) There is a significant increase in the zwitterionic character with a charge of +0.50 on the $PH_3$ group and a charge of −0.50 on the $CH_2$ group in the ylide. (2) There is a significant increase in the d orbital population upon formation of the ylide. This is required for the formation of hypervalent bonding leading to the short P–C bond. (3) There is a large increase in the dipole moment ($\mu$) on ylide formation in accord with the large charge separation. (4) The HOMO is significantly destabilized in the ylide, which is consistent with both the large energy difference between the ylide and the phosphine and the formation of a carbanionic center.

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(41) Lias, S. G.; Karpas, Z.; Liebman, J. F. *J. Am. Chem. Soc.* **1985**, *107*, 6089.

(42) The $\Delta H_f°(:C(CF_3)_2)(^1A_1)$ also can be evaluated from triplet energies and then corrected to the singlet from $\Delta E$(S–T) given in ref 26. This gives $\Delta H_f°$ = −203.7 kcal/mol.

(43) Correlation corrections to $\Delta E$(rxn 1) have been determined at the GVB+POL-CI level for $H_2PCH_3$, $H_2NCH_3$, $HSCH_3$, and $HOCH_3$.[1b] The largest corrections to $\Delta E$(SCF) are 5 kcal/mol (decrease) for $H_2PCH_3$ isomerization and 6 kcal/mol (increase) for $HOCH_3$ isomerization. Correlation corrections for eq 1 (X = Y = H) are −3.0 kcal/mol at the MP-2 level, giving $\Delta E$ = 53.0 kcal/mol. The $\Delta$ZPE correction is small (−1.1 kcal/mol), giving $\Delta H$ = 51.9 kcal/mol. For X = H, Y = F, the MP-2 correction is −3.4 kcal/mol, giving $\Delta E$ = 63.9 kcal/mol, and the $\Delta$ZPE correction is only −2.1 kcal/mol, giving $\Delta H$ = 61.8 kcal/mol. A similar result would be expected for the case X = Y = $CF_3$, which is strongly bound. The correlation corrections thus do not significantly change our results. The MP-2 calculations were done with the program GRADSCF (A. Komornicki, Polyatomics Research).

(44) The similarity of $\Delta E$(rxn 2) values for the triplet carbenes (Table III) may be fortuitous, or it may indicate that the triplet carbenes all have comparable inherent stabilities. Further work is needed to clarify this result.

(45) The geometry of the dissociated structure for $H_3PCF_2$ is consistent with earlier results[4e] that showed dissociation of $H_3PCH_2$ to $H_3P$ and $:CH_2(^1A_1)$ occurs by a rock of the carbene by which the two nominal lone pairs avoid each other. Furthermore, there is no barrier to dissociation beyond the endoergicity if the rock occurs. It similarly has been shown that there are essentially no barriers beyond the endoergicity for the process $H_2SCH_2 \rightarrow H_2S + :CH_2(^1A_1)$.[2b] We do not expect any significant energy barrier to complete dissociation of $H_2PCF_2$, other than the small endogericity.

(46) Marynick, D. S. *J. Mol. Struct.* **1982**, *87*, 161.

(47) Spitznagel, G. W.; Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Comput. Chem.* **1982**, *3*, 363.

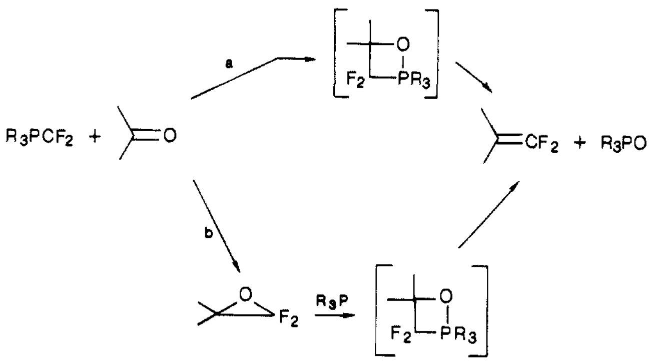
(48) Marynick, D. S.; Dixon, D. A. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 410.

**Table IV.** Molecular and Electronic Properties of Phosphines and Ylides

| molecule | $q$(P)[a] | $q$($P_{grp}$)[b] | $q$(C)[a] | $q$($C_{grp}$)[b] | $q$($P_d$)[c] | $\mu$ (D)[d] | HOMO (eV)[e] |
|---|---|---|---|---|---|---|---|
| $PH_2CH_3$ | 0.14 | 0.14 | -0.75 | -0.14 | 0.19 | 1.19 | 9.80 |
| $PH_3CH_2$ | 0.48 | 0.50 | -0.90 | -0.50 | 0.37 | 2.86 | 7.71 |
| $PH_2CH_2F$ | 0.13 | 0.17 | -0.26 | -0.17 | 0.20 | 1.34 | 10.51 |
| $PH_3CHF$ | 0.42 | 0.52 | -0.35 | -0.52 | 0.36 | 4.73 | 8.12 |
| $PH_2CHF_2$ | 0.15 | 0.19 | 0.12 | -0.19 | 0.20 | 3.03 | 11.00 |
| $PH_3CF_2$ | -0.05 | 0.01 | 0.23 | -0.01 | 0.20 | 0.88 | 10.52 |
| $PH_2CH(CF_3)_2$ | 0.22 | 0.34 | -0.62 | -0.34 | 0.19 | 3.99 | 11.56 |
| $PH_3C(CF_3)_2$ | 0.34 | 0.77 | -0.57 | -0.77 | 0.36 | 8.30 | 10.62 |

[a] Atomic charge. [b] Group charge. Evaluated by adding the hydrogen charges to the phosphorus. The group charge on C is obtained from the negative of the P group charge. [c] d population on phosphorus. [d] Dipole moment in debye. [e] Highest occupied molecular orbital in electron volts.

**Scheme I**



The ylide $H_3PCHF$ shows an even larger change in dipole moment than $H_3PCH_2$ upon isomerization, although the effective charge separation in the two ylides is quite similar. For $H_3PCHF$ there is a significant amount of negative charge delocalized to the fluorine and thus the center of negative charge is displaced away from the phosphorus. This creates a larger distance ($r$) between the positive and negative charges, and since $\mu\ \alpha\ r$, the dipole is larger. The change in HOMO energies is even larger for $H_3PCHF$, although its HOMO is more stable than that for $H_3PCH_2$. The larger change is consistent with the larger value for $\Delta E$(rxn 1) for $PH_3CHF$, whereas the more stable HOMO is consistent with the delocalization of negative charge to the fluorine.

The most stable ylide with respect to its isomeric phosphine is $H_3PC(CF_3)_2$. For this ylide, we find the largest charge separation, +0.77e on the $PH_3$ group and -0.77e on the $C(CF_3)_2$ group, and the largest absolute dipole. We also find the largest change in dipole and the least amount of destabilization of the HOMO. These are all consistent with $H_3PC(CF_3)_2$ having the lowest value for $\Delta E$(rxn 1). The $CF_3$ groups are better able to stabilize the negative charge than H or F.[49] The d orbital populations do not change for the bound ylides which shows that only a certain amount of hypervalent character can be observed at the phosphous.

The ylide $H_3PCF_2$ does not show any of these trends. The charge separation is approximately zero and is consistent with formation of only weakly associated $PH_3$ and :$CF_2$ fragments. The overall dipole moment is also very small and, in fact, is lower than that for the neutral phosphine. The HOMO is only slightly destabilized. Finally, there is no change in the amount of d orbital participation on P, which indicates that no hypervalent bond is formed. These results are consistent with our energetic and geometric results.

**Concluding Remarks.** The present study provides a coherent picture of the effects of fluorine substitution on the structure and stability of phosphonium ylides. The most striking results are the unique structure of $H_3PCF_2$ and its low binding energy for dissociation to $H_3P$ and :$CF_2$ ($\leq$1.2 kcal/mol). Its lability contrasts with that of either the parent $H_3PCH_2$ ylide or $H_3PC(CF_3)_2$, which have binding energies of over 50 kcal/mol. It therefore is most unlikely that thermal fragmentations of methylene or hexafluoroisopropylidene ylides into the corresponding phosphine and carbene can be observed experimentally in solution, although photochemical fragmentations may be possible.[50] Our calculations also predict that dissociation of $H_3PCHF$ into $H_3P$ and :CHF is endothermic, but by at most only 16.6 kcal/mol. It therefore may be possible to thermally generate :CHF in solution from $R_3PCHF$ derivatives, and experiments like those used to show the dissociation of $R_3PCF_2$ into $R_3P$ and :$CF_2$[19] may prove to be equally fruitful for $R_3PCHF$.

Our calculations show that the structure of $H_3PCF_2$ is entirely different from that of other phosphonium ylides. Its weakly associated $H_3P\cdots{:}CF_2$ ($^1A_1$) structure and its low binding energy readily explain the observed formation of :$CF_2$ from $R_3PCF_2$ ylides in solution,[19] but these properties raise some interesting questions about other known $R_3PCF_2$ chemistry. When generated in situ with many ketones and aldehydes, $R_3PCF_2$ is an efficient Wittig olefination agent.[11] Since $R_3PCF_2$ has no $R_3P^+$–$CF_2^-$ zwitterionic character, or any other properties of traditional Wittig reagents, why does it exhibit typical Wittig chemistry? The procedures used to generate $R_3PCF_2$ in situ suggest one possible explanation. Since all methods involve either dehalogenation or dehydrohalogenation of $R_3P^+CF_2X\ Y^-$ salts,[11] or decarboxylation of $R_3P^+$-$CF_2CO_2^-$ salts,[51] a short-lived $R_3P^+$–$CF_2^-$ species that can undergo typical Wittig chemistry may be produced initially, but in the absence of a reactant it rapidly converts to $R_3P\cdots{:}CF_2$ and dissociates. Moreover, our calculations apply to the gas phase only and, in the polar media normally used to generate $R_3PCF_2$, a transient $R_3P^+$–$CF_2^-$ zwitterionic species would be stabilized by solvation. Another and more interesting possibility is that Wittig reactions of $R_3PCF_2$ proceed by a mechanism which is different from that of other ylides. Instead of reacting with a carbonyl compound to directly produce the classical betaine intermediate (Scheme Ia), $R_3PCF_2$ conceivably could react via initial formation of a 2,2-difluoroepoxide, followed by phosphine-mediated deoxygenation to give 1,1-difluoroalkene product (Scheme Ib). There is ample precedent for the second step,[52] and :$CF_2$ additions at elevated temperatures to fluorinated carbonyl compounds such as $CF_3COF$[53] and $CF_3COCF_3$[54] to give epoxides have been reported. Whether :$CF_2$ can similarly add at modest temperatures to the hydrocarbon or partially fluorinated ketones and aldehydes that undergo Wittig reactions with $R_3PCF_2$, however, remains to be tested experimentally.

**Registry No.** $H_2PCH_3$, 593-54-4; $H_2PCH_2F$, 98509-58-1; $H_2PCHF_2$, 97523-71-2; $H_2PCH(CF_3)_2$, 104575-62-4; $H_3PCH_2$, 36429-11-5; $H_3PCHF$, 81938-16-1; $H_3PCF_2$, 104575-63-5; $H_3PC(CF_3)_2$, 104575-64-6; $PH_3$, 7803-51-2; $CH_4$, 74-82-8; $CH_3F$, 593-53-3; $CH_2F_2$, 75-10-5; $CH_3CH_3$, 74-84-0; $CFH_2CH_3$, 353-36-6; $CF_2HCH_3$, 75-37-6; $CH_2(CF_3)_2$, 690-39-1; $CF_2(CF_3)_2$, 76-19-7.

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