Gas-Phase Properties and Reactivities of Phospholide and Arsolide Anions

Lee S. Sunderlin,[†] Dimitra Panu,[‡] Dhananjay B. Puranik,[‡] Arthur J. Ashe, III,[*,‡] and Robert R. Squires[*,†]

Departments of Chemistry, Purdue University, West Lafayette, Indiana 47907, and University of Michigan, Ann Arbor, Michigan 48109

Received July 1, 1994[⊗]

The aromatic anions phospholide and arsolide have been generated in the gas phase at room temperature via the reaction of hydroxide ion with 1-*tert*-butylphosphole and 1-*tert*-butylarsole, respectively. The acid–base properties and reactivity of the ions were investigated with a flowing afterglow–triple quadrupole instrument. The proton affinities of both phospholide and arsolide have been determined from bracketing experiments to be 338 ± 3 kcal/mol. Exchange of two hydrogens for deuterium occurs in reactions of phospholide anion with FCH_2COOD. In contrast, no H/D exchange occurs in reactions of arsolide ion with FCH_2COOD, nor does it occur in reactions between pyrrolide anion and CF_3CH_2OD. These results are interpreted in terms of kinetic protonation of the heteroatom in all three anions, with exchange in the phospholide anion occurring by slow, reversible [1,5]-hydrogen shifts. All three heterocyclopentadienides are found to be relatively unreactive under flowing-afterglow conditions, exhibiting only slow clustering or addition reactions with polar, electrophilic reagents and electron transfer to NO_2. *Ab initio* molecular orbital calculations performed on the isomeric C_4H_5X (X = N, P) species indicate that 2*H*-phosphole and 3*H*-phosphole are 7.8 and 4.0 kcal/mol more stable than 1*H*-phosphole, respectively, while 2*H*-pyrrole and 3*H*-pyrrole are 11.5 and 13.0 kcal/mol less stable than 1*H*-pyrrole. Calculations on the corresponding $C_4H_4X^-$ (X = N, P) conjugate base anions predict proton affinities at the 2-position of phospholide and at the nitrogen atom of pyrrolide of 341.4 and 358.6 kcal/mol, respectively, in good agreement with the experimental data. The gas-phase acidities and relative stabilities of the nitrogen, phosphorus, and arsenic heteroles are discussed in terms of the calculated electronic and geometric structures.

Heteroles (**1a**–**5a**) and heterocyclopentadienides (**1d**–**5d**) of the group 15 elements are of considerable interest for the study of π-bonding between carbon and the main group elements (Scheme 1). Although pyrrole (**1a**) is certainly aromatic,[1] structural data on derivatives of the heavier heteroles **2a**,[2] **3a**,[3] **4a**,[4] and **5a**[5] indicate little π-conjugation involving the heteroatoms. In contrast, the structures of transition metal π-bonded derivatives of **2d**,[6] **3d**,[7] **4d**,[8] and **5d**[5,9] show that all of the heterocyclopentadienides have aromatic character.

The high acidity of cyclopentadiene (**6a**) derives from its energetically favorable conversion to the aromatic cyclopentadienide (**6d**). In the same manner, the acidities of the nonaromatic heteroles **2a**–**5a** are expected to be high, since removal of the 1*H* proton serves to convert them to aromatic anions (**2d**–**5d**, respectively). Indeed, it can be argued that the pK_a values of **2a**–**5a** (relative to suitable model compounds) could serve as thermodynamic measures of their delocalization energies. Unfortunately, measurement of the pK_a values in solution is complicated by the lability of the 1*H*-heteroles. Derivatives of 1*H*-phosphole (**2a**)[10] and 1*H*-arsole (**3a**)[11] rearrange to their equally labile 2*H* isomers (**2b** and **3b**, respectively), which form dimers (**7**) or other products.

In order to circumvent these difficulties, we have measured the gas-phase proton affinities of anions **2d** and **3d** using the bracketing method in a flowing-afterglow apparatus. To aid in the interpretation of the results, we have also performed *ab initio* molecular orbital calculations on the structures and energies of **1a**–**d** and **2a**–**d**. While this paper was in preparation, a detailed computational study of the structures, energetics, and rearrangement barriers in **1a**–**c** and in **2a**–**c** appeared that used theoretical methods similar to those

---

[†] Purdue University.

[‡] University of Michigan.

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1994.

(1) Chadwick, D. J. Pyrroles and their Benzo Derivatives: (i) Structure. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon Press: Oxford, U.K., 1984; Vol. 4, pp 155–200.

(2) Mathey, F. *Chem. Rev.* **1988**, *88*, 429.

(3) Ashe, A. J., III; Butler, W. M.; Diephouse, T. R. *Organometallics* **1983**, *2*, 1005.

(4) Ashe, A. J., III; Butler, W.; Diephouse, T. R. *J. Am. Chem. Soc.* **1981**, *103*, 207.

(5) Ashe, A. J., III; Kampf, J. W.; Puranik, D. B.; Al-Taweel, S. M. *Organometallics* **1992**, *11*, 2743.

(6) de Lauzon, G.; Deschamps, B.; Fischer, J.; Mathey, F.; Mitschler, A. *J. Am. Chem. Soc.* **1980**, *102*, 994. Mathey, F.; Mitschler, A.; Weiss, R. *J. Am. Chem. Soc.* **1976**, *99*, 3537.

(7) Chiche, L.; Galy, J.; Thiollet, G.; Mathey, F. *Acta Crystallogr.* **1980**, *B36*, 1344.

(8) (a) Ashe, A. J., III; Diephouse, T. R.; Kampf, J. W.; Al-Taweel, S. M. *Organometallics* **1991**, *10*, 2068. (b) Ashe, A. J., III; Kampf, J. W.; Al-Taweel, S. M. *Organometallics* **1992**, *11*, 1491.

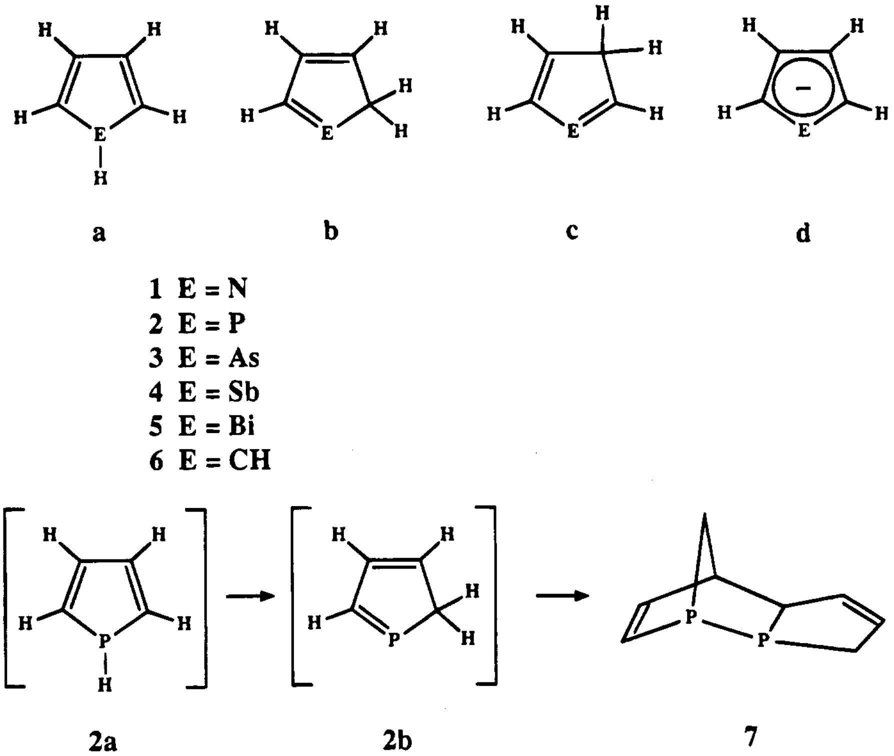
(9) Ashe, A. J., III; Kampf, J. W.; Al-Taweel, S. M. *J. Am. Chem. Soc.* **1992**, *114*, 372.

(10) Mathey, F. *Acc. Chem. Res.* **1992**, *25*, 90.

(11) Sendlinger, S. C.; Haggerty, B. S.; Rheingold, A. L.; Theopold, K. H. *Chem. Ber.* **1991**, *124*, 2453.

0276-7333/94/2313-4732$04.50/0

Scheme 1

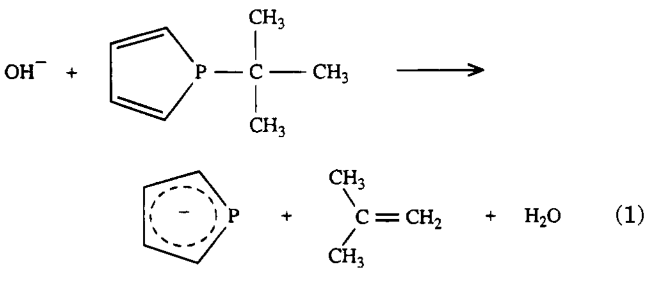


1 E = N
2 E = P
3 E = As
4 E = Sb
5 E = Bi
6 E = CH

employed in the present work.[12] Because the focus in this study is on the properties of the anions, and because of the slight differences in the theoretical levels used and the results obtained, we present here the full details of our calculations and a brief comparison with the results of the earlier investigation.

Experimental Section

All experiments were carried out at room temperature (296 ± 2 K) in a flowing-afterglow–triple-quadrupole apparatus.[13] The pressure and flow rate of the helium buffer gas used was 0.4 Torr and 190 STP cm^3/s, respectively. Hydroxide ions were formed at the upstream end of the flowing afterglow by electron ionization of a N_2O/CH_4 mixture. Phospholide anion was formed as the major ionic product of the elimination reaction between OH^- and 1-*tert*-butylphosphole (reaction 1).



(1)

Arsolide anion was formed as the major product of an analogous reaction with 1–*tert*-butylarsole. These precursors were added 25 cm downstream from the electron gun to avoid possible rearrangement reactions that could occur under direct electron impact. Neutral reagents were added through variable-flow metering valves located downstream from the inlet where the phosphole or arsole was added. In most cases it was necessary to flow helium over the low-volatility samples to obtain a sufficient flow rate of neutral reagent, and in some cases, it was necessary to replace the metering valve with a high-conductance on/off valve. It was not generally possible to measure directly the flow rates of these neutral reagents because of their low volatility. However, rough estimates of the flow rates could be obtained by following the extent of depletion of the hydroxide ion signal intensity in the absence of the phosphole or arsole reagent.

Materials. CF_3CH_2OD (78% d_1) was synthesized by the sequential reaction of trifluoroethanol with sodium and D_2O.[14] FCH_2COOD (95% d_1) was synthesized by a base-catalyzed exchange reaction between FCH_2COOH and D_2O. The indicated isotopic purities of these compounds were determined from the cluster ion signals observed in the negative ion mass spectra. Pyrrole was obtained from Eastman Organic Chemicals and distilled prior to use. All other liquid reagents were obtained from commercial sources and used as received except for freeze–pump–thaw cycles. Helium (99.995%), CH_4 (99.99%), and O_2 (99.994%) were obtained from Airco; N_2O (99%) and SO_2 (99.98%) were obtained from Matheson; NO (99%) and NO_2 (99.5%) were obtained from Liquid Carbonic. 1-*tert*-Butylphosphole and 1-*tert*-butylarsole were prepared by an adaptation of the route used to prepare the corresponding phenyl compounds described below.[15]

1-*tert*-Butylphosphole. A solution of 3.5 M *n*-butyllithium in hexane (5 mL, 17.5 mmol) was added to *tert*-butylphosphine[16] (2.30 g, 25.5 mmol) in 2.50 mL of ether. The orange-red solution was stirred at 25 °C for 16 h, after which a mixture of isomeric 1,4-dichloro-1,3-butadienes[17] (3.0 g, 24 mmol) was added. The reaction mixture was heated to reflux for 2 h, and after it was cooled to 25 °C, it was stirred for 16 h. The resulting brown solution was subject to pot-to-pot distillation,

---

[12] Bachrach, S. M. *J. Org. Chem.* **1993**, *58*, 5414.

[13] Marinelli, P. J.; Paulino, J. A.; Sunderlin, L. S.; Wenthold, P. G.; Poutsma, J. C.; Squires, R. R. *Int. J. Mass Spectrom. Ion Processes* **1994**, *130*, 89.

[14] Borneman, E. H., Ph.D. Thesis, Purdue University, 1952.

[15] Ashe, A. J., III; Mahmoud, S.; Elschenbroich, C.; Wünsch, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 229.

[16] Müller, M.; Vahrenkamp, H. *Chem. Ber.* **1983**, *116*, 2311.

[17] Criegee, R.; Hörauf, W.; Schellenberg, W. D. *Chem. Ber.* **1953**, *86*, 126.

and the distillate was fractionated through a Vigreux column to remove most of the ether. The residue was purified by GC (Apiezon L column), affording 160 mg (5%) of 1-*tert*-butylphosphole as a colorless oil. ^{1}H NMR (CDCl$_3$): δ 1.17 (d, J = 13.7 Hz, 9H), 6.739 (H2), 7.007 (H3) A_2B_2 pattern (J_{12} = 37.0 Hz, J_{13} = 13.7 Hz, J_{23} = 7.2 Hz, J_{24} = 1.1 Hz, J_{25} = 3.0 Hz, J_{34} = 2.0 Hz, (4H)). ^{13}C NMR (CDCl$_3$): δ 29.43 (d, J = 12 Hz, CH$_3$), 33.56 (d, J = 7 Hz, C), 131.93 (d, J = 8 Hz, CH), 137.04 (d, J = 5 Hz, CH). ^{31}P NMR (CDCl$_3$): δ 40.0. Exact mass (EI) mass spectrum: calculated for $C_8H_{13}P$ 140.0755, found 140.0755.

1-*tert*-Butylarsole. A solution of 3.5 M *n*-butyllithium in hexane (12 mL, 42 mmol) was added to *tert*-butylarsine[18] (2.7 g, 20 mmol) in 250 mL of ether. The orange-red solution was stirred at 25 °C for 16 h, after which a mixture of isomeric 1,4-dichloro-1,3-butadienes (2.0 g, 1.6 mmol) was added. This reaction mixture was heated to reflux for 2 h, and after it was cooled to 25 °C, it was stirred for 16 h. Removal of solvent under reduced pressure left a brown residue, which was subject to pot-to-pot distillation (50 °C, 0.1 Torr), affording a colorless liquid. Final purification was effected by preparative GC (Apiezon L column), giving 280 mg (10%) of 1-*tert*-butylarsole as a colorless air-sensitive liquid. ^{1}H NMR (CDCl$_3$): δ 1.21 (s, 9H), 6.949, 7.112 (A_2B_2 pattern, J_{23} = 7.5 Hz, J_{24} = 1.0 Hz, J_{25} = 3.0 Hz, J_{34} = 2.0 Hz, (4H)). ^{13}C NMR (CDCl$_3$): δ 30.26 (CH$_3$), 38.30 (C), 139.18, 139.41 (CH). Exact mass (EI) mass spectrum: calculated for $C_8H_{13}As$ 184.0233, found 184.0232.

Computational Methods. The energetics for various reactions involving the phospholes, pyrroles, and their conjugate base anions were evaluated at different levels of theory using the GAUSSIAN 90[19] and 92[20] packages of *ab initio* MO programs on a DEC VAXstation 3200. Complete geometry optimizations were carried out using analytically evaluated energy gradients, and all stationary points were verified to be true minima by examination of the matrix of computed force constants. For each of the ions and neutral molecules in this study, geometries and vibrational frequencies were obtained with a 6-31+G(d) basis set that incorporates polarization functions and additional diffuse functions for each heavy atom. Correlation-corrected single-point energies were computed with the near-triple-ζ 6-311+G(d) basis set using third-order Møller–Plesset perturbation theory (frozen core) (*i.e.*, MP3/6-311+G(d)//6-31+G(d)). The calculated energy changes (ΔE_{TOT}) for all reactions were converted to 298 K enthalpies by including the standard zero-point energy, temperature, and work terms given by eq 2.[21] The calculated vibrational frequencies were scaled by a factor of 0.9.[22]

$$\Delta H_{298} = \Delta E_{\mathrm{TOT}} + \Delta E_{\mathrm{vib}} + \Delta(\Delta E_{\mathrm{vib}})_{298} + \Delta E_{\mathrm{rot}} + \Delta E_{\mathrm{trans}} + \Delta PV \quad (2)$$

Results

Proton Affinity Bracketing. The proton affinity of the phospholide anion was determined by monitoring its reactivity with a series of neutral reference acids (HA) with known gas-phase acidities, *i.e.*, by a bracketing procedure.[23] Reaction 3 should be rapid under the

$$C_4H_4P^- + HA \rightarrow C_4H_5P + A^- \quad (3)$$

thermal conditions of the flow tube only if the reaction is exothermic. If proton transfer is thermoneutral or endothermic by a small amount (up to a few kcal/mol), then reaction can still be observed, albeit with a lower rate.[24] If the reaction is significantly endothermic, then proton transfer will not occur on an observable time scale. A summary of the results is provided in Table 1. $C_4H_4P^-$ reacts rapidly with 2-chloropropionic acid and chloroacetic acid *via* proton transfer, providing a lower limit on $\Delta G_{\mathrm{acid}}(C_4H_5P)$ of 330.4 ± 2.0 kcal/mol. Very slow depletion of the $C_4H_4P^-$ signal is observed with fluoroacetic acid, giving an upper limit to $\Delta G_{\mathrm{acid}}(C_4H_5P)$ of 331.6 ± 2.0 kcal/mol. No reaction is observed with less acidic reference acids. These results can be used to assign $\Delta G_{\mathrm{acid}}(C_4H_5P) = 331 \pm 3$ kcal/mol. Conversion of the bracketed ΔG_{acid} value to the corresponding enthalpy term, ΔH_{acid}, requires an estimate of the entropy contribution. This can be derived from the relation $\Delta S_{\mathrm{acid}} = \Delta S_{\mathrm{rot}} + S(H^+)$,[25] where ΔS_{rot} is the change in rotational entropy and $S(H^+)$ is the absolute entropy of the proton (26.0 eu).[26] The phospholide anion is a planar species with C_{2v} symmetry ($\sigma = 2$), while all three neutral phosphole tautomers possess C_s symmetry ($\sigma = 1$). Therefore, ΔS_{acid} for the phosphole system amounts to $R \ln(1/2) + 26.0$ eu = 24.6 eu, and at 298 K $\Delta H_{\mathrm{acid}}(C_4H_5P)$ is determined to be 338 ± 3 kcal/mol.

Table 1. Summary of Proton Affinity Bracketing Results for $C_4H_4P^-$ and $C_4H_4As^-$ [a]

HA	$\Delta G_{\mathrm{acid}}(\mathrm{HA})$[b]	$C_4H_4P^-$ [c]	$C_4H_4As^-$ [c]
$(CH_3)_2CHCOOH$	339.0 ± 2.0	−	
HCOOH	338.3 ± 2.0	−	
o-chlorophenol	337.1 ± 2.0	−	
p-chlorophenol	336.2 ± 2.0	−	−
CH_3OCH_2COOH	335.3 ± 2.0	−	−
C_6H_5SH	333.7 ± 2.0	slow[d]	slow[d]
FCH_2COOH	331.6 ± 2.0	slow[d]	slow[d]
$CH_3CHClCOOH$	330.4 ± 2.0	+	+
$ClCH_2COOH$	329.0 ± 2.0	+	+
$BrCH_2COOH$	328.2 ± 2.0	+	+
$F_2CHCOOH$	323.8 ± 2.0	+	+

[a] All reactions carried out in the helium flow reactor at 298 K. [b] Gas-phase acidity in kcal/mol.[23] [c] + and − correspond to observing and not observing proton transfer, respectively. [d] By "slow" it is meant tht while some proton transfer takes place, it does so with an apparent rate that is much less than that for the other proton transferse under conditions of comparable neutral flow rate (ca. 0.1 STP cm^3/s).

The nonoccurrence of reaction 3 with a reference acid could be due to kinetic, rather than thermodynamic, constraints. With bracketing procedures this can often be tested by examining the reverse proton transfer reactions involving the corresponding conjugate acid and various reference bases. However, this is not possible in the present case because of the unavailability of the

---

(18) Becker, G.; Gutekunst, G.; Wessely, H. J. *Z. Anorg. Allg. Chem.* **1980**, *462*, 113.

(19) Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M. A.; Binkley, J. S.; Gonzales, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian 90; Gaussian, Inc.: Pittsburgh, PA, 1990.

(20) Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Gill, P. M.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Replogle, E. S.; Gomberts, R.; Andres, J. L.; Raghavachari, K.; Robb, M. A.; Binkley, J. S.; Gonzales, C.; Defrees, D. J.; Fox, D. J.; Baker, J.; Martin, R. L.; Pople, J. A. Gaussian 92, Revision A; Gaussian, Inc.: Pittsburgh, PA, 1992.

(21) Del Bene, J. F.; Metee, H. D.; Frisch, M. J.; Luke, B. T.; Pople, J. A. *J. Phys. Chem.* **1983**, *87*, 3279.

(22) Hout, R. F., Jr.; Levi, B. A.; Hehre, W. J. *J. Comput. Chem.* **1982**, *3*, 234.

(23) Lias, S. G.; Bartmess, J. E.; Liebmann, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1. Updated in: Bartmess, J. E. NIST Std. Ref. Database 19B (Negative Ion Energetics Database Ver. 3.00), 1993.

(24) Meot-Ner, M. *J. Am. Chem. Soc.* **1982**, *104*, 5.

(25) Bartmess, J. E.; McIver, R. T., Jr. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 11.

(26) Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1 (JANAF Tables).

extremely reactive unsubstituted phospholes as neutral reagents. Nevertheless, the reference acids used in the present study are known to be kinetically well-behaved in proton transfer reactions.[27] Thus, there is little possibility of a barrier to proton transfer for the reactions examined. However, because the reference acids used in this study are highly polar species that tend to form clusters with anions under the relatively high pressure conditions in the flowing afterglow, it was necessary to verify that the observed depletion of the $C_4H_4P^-$ signal was due to proton transfer from the monomer of the neutral acid, rather than neutral dimers, trimers, etc. This was accomplished by monitoring the $C_4H_4P^-(HA)_n$ and $A^-(HA)_n$ signals that were in some cases present in the mass spectrum and confirming that their increase in intensity with added neutral reagent was significantly less than the observed depletion of the $C_4H_4P^-$ signal intensity.

Nearly identical bracketing results were obtained with arsolide anion (Table 1). Arsolide reacts rapidly with 2-chloropropionic acid and chloroacetic acid, but with increasing slowness with weaker acids, until no proton transfer reaction is observed with methoxyacetic acid. These results suggest the same effective basicity for arsolide ion as phospholide ion, *i.e.*, $\Delta G_{\text{acid}}(C_4H_5As) = 331 \pm 3$ kcal/mol. An entropy calculation identical with that for phosphole gives $\Delta H_{\text{acid}}(C_4H_5As) = 338 \pm 3$ kcal/mol.

In order to examine the possibilities for carbon protonation of $C_4H_4P^-$ and $C_4H_4As^-$ by the reference acids, H/D exchange reactions were attempted with selected deuterated species. H/D exchange can occur during a single ion–molecule encounter by D^+ transfer to an atom of the negative ion that has one or more hydrogens attached (such as one of the carbon atoms in the $C_4H_4X^-$ (X = N, P, As) species), followed by the back-transfer of H^+.[28] If the deuterated compound is a stronger acid than the conjugate acid of the anion under examination, then deuteron transfer will occur rather than H/D exchange. If the deuterated reagent is a significantly weaker acid, then D^+ transfer will not occur within the ion-molecule complex and no exchange will be observed. Because fluoroacetic acid is just slightly less acidic than phosphole and arsole (*cf.* Table 1), FCH_2COOD is a good candidate for examining H/D exchange reactions. Indeed, in addition to slow deuteron transfer, forming FCH_2COO^-, a maximum of two of the hydrogens in the phospholide ion are observed to exchange for deuterium with added FCH_2COOD. This must be due to either direct or indirect deuteron transfer from the acid molecules to two of the carbon sites of phospholide, at least during some of the ion–molecule collisions. Which of the two pairs of different carbon sites in $C_4H_4P^-$ are involved cannot be determined from the present experiments, but the calculations described below suggest that the 2*H* sites are the most likely (*vide infra*). As the flow rate of FCH_2COOD is increased, the total signal for the phospholide ions is depleted by deuteron transfer. Thus, it is possible that exchange is occurring at the remaining two carbon sites, but with a maximum rate that is significantly lower than that for the first two exchanges.

Table 2. Calculated Total Energies (au)

	species	$-E_{\text{TOT}}$- (6-31+G(d))	ZPE[a]	$-E_{\text{TOT}}$- (MP3/6-311++G(d))
2a	1*H*-phosphole C_s	496.064 252	45.5	495.780 502
2b	2*H*-phosphole C_s	495.066 129	46.7	495.794 741
2c	3*H*-phosphole C_s	495.061 356	46.6	495.788 564
2d	phospholide anion	494.509 080	39.2	495.240 707
2e	TS phosphole inversion C_{2v}	495.024 632	44.0	495.750 479
1a	pyrrole C_{2v}	208.816 737	50.1	209.578 777
1b	2*H*-pyrrole C_s	208.800 352	49.7	209.559 798
1c	3*H*-pyrrole C_s	208.797 479	49.4	209.557 082
1d	pyrrolide anion C_{2v}	208.225 998	41.4	208.995 717

[a] Zero point energies in kcal/mol; all frequencies scaled by 0.9.

In contrast, no exchange is observed in the reaction of the arsolide anion with FCH_2COOD, suggesting that either the carbon sites in this ion are substantially less basic than the arsenic site or some other kinetic constraint exists that inhibits exchange. A similar experiment was carried out with CF_3CH_2OD and pyrrolide ions. Trifluoroethanol is slightly less acidic than pyrrole ($\Delta G_{\text{acid}}(CF_3CH_2OH) = 354.1 \pm 2.0$ kcal/mol; $\Delta G_{\text{acid}}(\text{pyrrole}) = 350.9 \pm 2.0$ kcal/mol[23]). No exchange occurs in this case. This is consistent with the fact that the carbon sites in pyrrolide ion are much less basic than the nitrogen site, as discussed below.

The reactivity of the pyrrolide, phospholide, and arsolide anions was examined with a variety of neutral compounds typically used in negative ion studies.[29] The list of neutral reagents includes O_2, SO_2, CS_2, $Fe(CO)_5$, NO_2, NO, CH_2I_2,[30] hexafluorobenzene, and alkyl nitrites. The only clear-cut bimolecular reaction observed was electron transfer from pyrrolide, phospholide, and arsolide to NO_2.[31] The electron transfer observed with NO_2 indicates that $EA(C_4H_4X, X = N, P, As) \leq EA(NO_2) = 2.27$ eV.[32] This is at the low end of the reported range for the electron affinity of pyrrole, $EA(C_4H_4N) = 2.39 \pm 0.13$ eV, determined by electron photodetachment experiments.[33] In some cases, products were observed that corresponded to ion–molecule clustering or nucleophilic addition in the ions to the neutral reagent. The absolute rates of these reactions were not measured; however, adduct formation was apparently most rapid with C_6F_6 and SO_2. The low reactivity of $C_4H_4X^-$ (X = N, P, As) anions with these reagents is consistent with their low basicities.

Computational Results. The structures and energies of the phospholes and pyrroles and the corresponding conjugate base anions were investigated using a level of *ab initio* molecular orbital theory that should provide realistic estimates of the thermodynamic quantities measured in this study.[34] Total energies for each of the species examined are listed in Table 2, along with

---

[27] Gronert, S. *J. Am. Chem. Soc.* **1993**, *115*, 10258 and references therein.

[28] (a) Stewart, J. H.; Shapiro, R. H.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1977**, *99*, 7650. (b) Squires, R. R.; Bierbaum, V. M.; Grabowski, J. J.; DePuy, C. H. *J. Am. Chem. Soc.* **1983**, *105*, 5185.

[29] (a) DePuy, C. H.; Bierbaum, V. M. *Acc. Chem. Res.* **1981**, *14*, 146. (b) Nibbering, N. M. M. *Adv. Phys. Org. Chem.* **1988**, *24*, 1. (c) Squires, R. R. *Acc. Chem. Res.* **1992**, *25*, 461.

[30] The reaction between CH_2I_2 and $C_4H_4As^-$ was not examined due to the mass overlap of $C_4H_4As^-$ and I^- (*m/z* 127).

[31] Experimental studies of clustering energetics involving pyrrole are described in: Meot-Ner, M. *J. Am. Chem. Soc.* **1988**, *110*, 3858.

[32] Ervin, K. M.; Ho, J.; Lineberger, W. C. *J. Phys. Chem.* **1988**, *92*, 5405.

[33] Richardson, J. H.; Stephenson, L. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1975**, *97*, 1160.

[34] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

their zero-point energies derived from the scaled harmonic frequencies. The optimized geometries for each of the minimum energy species are specified in Table 3 and shown in Figure 1. The energetics of several reactions involving **1a**–**1d** and **2a**–**2e** have been evaluated from the theoretical data; these results are listed in Table 4. The enthalpy changes for some of the reactions calculated in ref 12 are also included for comparison.

Structures. 1*H*-Phosphole (**2a**) is a nonplanar molecule with a PH/ring bond angle of 102° and a CPC bond angle of 89°, *i.e.*, the phosphorus atom is strongly pyramidalized. This is the norm for trivalent phosphorus compounds: minimal s–p mixing results in a nearly pure 3s lone pair and 3pσ bonding orbitals.[35] The absence of π conjugation involving phosphorus is further indicated by the long P–C bonds (1.82 Å) that are nearly the same length as those in Me_3P (1.84 Å),[36] and C–C bond lengths in the dienyl moiety that are essentially the same as those in 1,3-butadiene (r_{12} = 1.341 Å; r_{23} = 1.463 Å).[37] For comparison, the greater extent of π conjugation in planar pyrrole (**1a**) and the 1*H*-phosphole inversion transition structure **2e** leads to shorter C–N and C–P bonds than in their saturated analogs and reduced bond length alternation in the dienyl moieties.

The *iso*-phospholes **2b**,**c** are calculated to have planar ring structures with similar P=C double bond distances near 1.67 Å and P–C single bond lengths in the range 1.83–1.87 Å. For comparison, the experimentally measured P=C bond length is 1.67 Å in CH_2=PH[38] and 1.69 Å in the more substituted derivative $(C_6H_5)_2C$=P-(C_9H_{11}).[39] High-level *ab initio* calculations find the bond length in CH_2=PH to be 1.65 Å.[40] As with 1*H*-phosphole (**2a**), the ring geometries of **2b**,**c** are dominated by the *ca.* 90° C–P=C bond angles, suggesting a low degree of s–p hybridization at the doubly bonded phosphorus atom and a nearly pure 3s lone pair.

Significant geometry changes accompany flattening of the phosphorus in the transition structure **2e** computed for P–H inversion in **2a**. The P–C bond lengths decrease by 0.1 Å, the P–H bond distance shrinks by 0.03 Å, and the C–C bond distances change by 4–5%, partially reflecting the onset of π-conjugation between the phosphorus 3p lone pair and the dienyl moiety. In order to accommodate the obligatory increase in s–p mixing at phosphorus in this planar structure, the CPC bond angle expands to 98°.

The structures computed for **2a**,**c** in this study are very similar to those obtained at the HF/6-31G(d) level of theory by Bachrach, at the HF/6-311G(d) level (for **2a**) by Hughes and Edgecombe,[41] and at the HF/3-21G-(d) level (for **2a**) by Baldridge and Gordon.[42] The optimized geometries obtained in ref 12 at the MP2/6-31G(d) level show less bond length alternation than in

Table 3. Calculated Geometries[a]

species	point group	bond lengths (Å)	bond angles (deg)[b]
2a	C_s	P_1C_2 1.824	$C_2P_1C_5$ 89.3
		C_2C_3 1.335	$P_1C_2C_3$ 111.2
		C_3C_4 1.471	$C_2C_3C_4$ 114.1
		P_1H 1.406	HP_1C_2 99.1
		C_2H 1.074	HC_2C_3 124.6
		C_3H 1.076	HC_3C_2 124.1
			$HP_1C_2C_3$ 102.9
2b	C_s	P_1C_2 1.868	$C_2P_1C_5$ 90.9
		C_2C_3 1.497	$P_1C_2C_3$ 106.7
		C_3C_4 1.335	$C_2C_3C_4$ 114.2
		C_4C_5 1.460	$C_3C_4C_5$ 113.4
		P_1C_5 1.674	$P_1C_5C_4$ 114.9
		C_2H 1.089	HC_2C_3 111.5
		C_3H 1.075	HC_3C_2 121.7
		C_4H 1.075	HC_4C_5 123.3
		C_5H 1.075	HC_5C_4 121.1
			$HC_2C_3C_4$ 120.7
2c	C_s	P_1C_2 1.689	$C_5P_1C_2$ 89.5
		C_2C_3 1.495	$P_1C_2C_3$ 115.8
		C_3C_4 1.501	$C_2C_3C_4$ 107.4
		C_4C_5 1.324	$C_3C_4C_5$ 115.3
		P_1C_5 1.888	$P_1C_5C_4$ 111.9
		C_2H 1.069	HC_2C_3 119.9
		C_3H 1.089	HC_3C_2 110.6
		C_4H 1.072	HC_4C_5 124.3
		C_5H 1.069	HC_5C_4 124.8
			$HC_3C_4C_5$ 121.1
2d	C_{2v}	P_1C_2 1.764	$C_2P_1C_5$ 89.9
		C_2C_3 1.382	$P_1C_2C_3$ 112.2
		C_3C_4 1.418	$C_2C_3C_4$ 112.9
		C_2H 1.078	HC_2C_3 123.2
		C_3H 1.080	HC_3C_2 124.0
2e	C_{2v}	P_1C_2 1.720	$C_2P_1C_5$ 98.2
		C_2C_3 1.375	$P_1C_2C_3$ 105.5
		C_3C_4 1.423	$C_2C_3C_4$ 115.3
		P_1H 1.374	HP_1C_2 130.9
		C_4H 1.070	HC_2C_3 126.5
		C_5H 1.074	HC_3C_2 122.3
1a	C_{2v}	N_1C_2 1.363	$C_2N_1C_5$ 109.5
		C_2C_3 1.361	$N_1C_2C_3$ 108.1
		C_3C_4 1.427	$C_2C_3C_4$ 107.1
		N_1H 0.993	HN_1C_2 125.2
		C_2H 1.070	HC_2C_3 130.7
		C_3H 1.071	HC_3C_2 126.0
1b	C_s	N_1C_2 1.451	$C_2N_1C_5$ 118.9
		C_2C_3 1.503	$N_1C_2C_3$ 117.4
		C_3C_4 1.329	$C_2C_3C_4$ 107.5
		C_4C_5 1.477	$C_3C_4C_5$ 105.9
		N_1C_5 1.264	$N_1C_5C_4$ 113.8
		C_2H 1.086	HC_2C_3 112.4
		C_3H 1.073	HC_3C_2 124.7
		C_4H 1.073	HC_4C_5 125.7
		C_5H 1.076	HC_5C_4 124.7
			$HC_2C_3C_4$ 119.5
1c	C_s	N_1C_2 1.265	$C_2N_1C_5$ 106.6
		C_2C_3 1.505	$N_1C_2C_3$ 113.8
		C_3C_4 1.502	$C_2C_3C_4$ 99.7
		C_4C_5 1.328	$C_3C_4C_5$ 107.1
		N_1C_2 1.422	$N_1C_5C_4$ 112.8
		C_2H 1.076	HC_2C_3 124.4
		C_3H 1.088	HC_3C_2 111.6
		C_4H 1.072	HC_4C_5 127.4
		C_5H 1.072	HC_5C_4 128.6
			$HC_3C_4C_5$ 118.6
1d	C_{2v}	N_1C_2 1.346	$C_2N_1C_5$ 105.4
		C_2C_3 1.392	$N_1C_2C_3$ 112.2
		C_3C_4 1.414	$C_2C_3C_4$ 105.1
		C_2H 1.078	HC_2C_3 127.3
		C_3H 1.077	HC_3C_2 127.2

[a] 6-31+G(d) basis set; all structures verified as true minima by computed force constants. [b] Four-atom entries correspond to dihedral angles.

---

(35) Emsley, J.; Hall, D. *The Chemistry of Phosphorus*; Wiley: New York, 1976.

(36) Bryan, P. S.; Kuczkowski, R. L. *J. Chem. Phys.* **1971**, *55*, 3049.

(37) Bock, C. W.; Panchenko, Y. N. *J. Mol. Struct.* **1989**, *187*, 69. See also: Wiberg, K. B.; Rosenberg, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 1509.

(38) Hopkinson, M. J.; Kroto, H. W.; Nixon, J. F.; Simmons, N. P. C. *J. Chem. Soc., Chem. Commun.* **1976**, 513.

(39) Van der Knaap, Th. A.; Klebach, Th. C.; Visser, F.; Bickelhaupt, F.; Ros, P.; Baerends, E. J.; Stam, C. H.; Konijn, M. *Tetrahedron* **1984**, *40*, 765.

(40) Schleyer, P. v. R.; Kost, D. *J. Am. Chem. Soc.* **1988**, *110*, 2105.

(41) Hughes, A. N.; Edgecombe, K. E. *Heterocycles* **1992**, *33*, 563.

(42) Baldridge, K. K.; Gordon, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 4204.

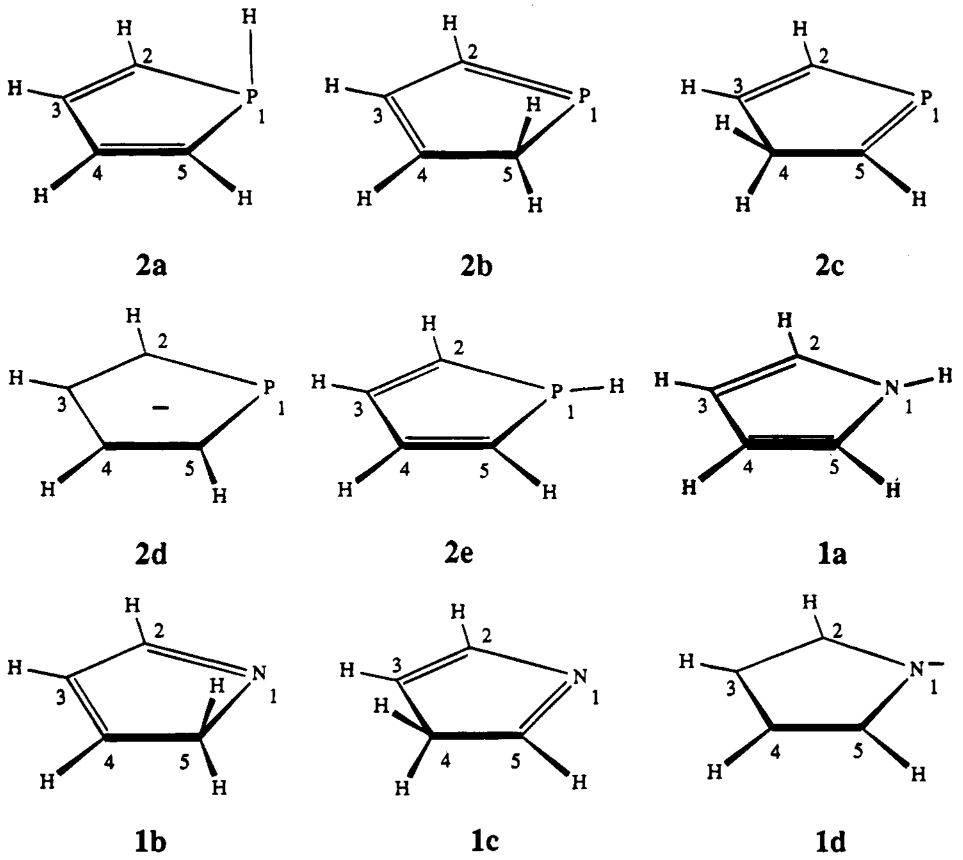

2a **2b** **2c**
2d **2e** **1a**
1b **1c** **1d**

Figure 1. Structures of isomeric phospholes and pyrroles and their conjugate base anions (cf. Table 3).

Table 4. Calculated Reaction Enthalpies (kcal/mol)[a]

reacn	ΔH_{298} (this work)	ΔH_{298} (ref 12)[c]
1*H*-phosphole (**2a**) → 2*H*-phosphole (**2b**)	−7.8	−6.5 (−7.0)[d]
1*H*-phosphole (**2a**) → 3*H*-phosphole (**2c**)	−4.0	−2.8
1*H*-phosphole (**2a**) → C_{2v} inversion TS (**2e**)[b]	18.9	
1*H*-phosphole (**2a**) → phospholide anion (**2d**) + H^+	333.6	
2*H*-phosphole (**2b**) → 3*H*-phosphole (**2c**)	3.8	3.7
2*H*-phosphole (**2b**) → phospholide anion (**2d**) + H^+	341.4	
3*H*-phosphole (**2c**) → phospholide anion (**2d**) + H^+	337.6	
pyrrole (**1a**) → 2*H*-pyrrole (**1b**)	11.5	13.0
pyrrole (**1a**) → 3*H*-pyrrole (**1c**)	13.0	15.2
pyrrole (**1a**) → pyrrolide anion (**1d**) + H^+	358.6	
2*H*-pyrrole (**1b**) → 3*H*-pyrrole (**1c**)	1.5	2.2
2*H*-pyrrole (**1b**) → pyrrolide anion (**1d**) + H^+	347.1	
3*H*-pyrrole (**1c**) → pyrrolide anion (**1d**) + H^+	345.6	

[a] Based on differences in calculated total energies (MP3) corrected to 298 K enthalpies; structures determined at the 6-31+G(d) level. [b] Transition state verified by 6-31+G(d) frequency analysis. [c] MP2/6-31G(d)//MP2/6-31G(d); corrected to 298 K enthalpies. [d] MP4SDQ/6-31G(d)//MP2/6-31G(d).

the HF geometries, and the structure for **2a** features a slightly puckered ring, with the phosphorus atom lying 0.18 Å above the plane of the dienyl moiety. The MP2 structure for **2a** is in generally better agreement with the X-ray structure reported for 1-benzylphosphole[43] than are the 6-31G(d) or 6-31+G(d) structures, suggesting that inclusion of electron correlation is necessary for accurate structural predictions.[44]

Deprotonation of **2a**, **2b**, or **2c** gives the phospholide anion structure **2d** that is quite similar to the phosphorus inversion transition structure **2e** in terms of the PC and CC bond lengths, but with a much reduced CPC bond angle of *ca.* 90°. This is due to the ability of the phosphorus atom to maintain π-bonding with the dienyl moiety and a pure 3s-type lone pair without any s−p hybridization. The 6-31G(d) structure for **2d** found in this work is similar to those obtained in earlier theoretical studies using semiempirical[45−47] and *ab initio*[48] MO methods, although a greater degree of bond length alternation is evident. For example, Malar[45] reports nearly identical CC bond distances of 1.403 Å, whereas they are calculated in this work to differ by more than 0.03 Å (Table 3). Although there are no experimental structural data for **2d** to compare with the calculated data, an X-ray diffraction structure is available for the lithiotetramethylethylenediamine salt of 2,3,4,5-tetra-

---

[43] Coggan, P.; Engel, J. F.; McPhail, A. T.; Quin, L. D. *J. Am. Chem. Soc.* **1970**, *92*, 5779.

[44] For earlier calculations on 1 at lower levels of theory, see ref 2 and references 8−10 in ref 12.

[45] Malar, E. J. P. *J. Org. Chem.* **1992**, *57*, 3694.

[46] Kaufman, G.; Mathey, F. *Phosphorus Relat. Group V Elem.* **1974**, *4*, 231.

[47] Guimon, C.; Pfister-Guillouzo, G.; Mathey, F. *Nouv. J. Chim.* **1974**, *3*, 725.

[48] Kostic, N. M.; Fenske, R. F. *Organometallics* **1983**, *2*, 1008.

methylphospholide.[49] It is noteworthy that the calculated ring bond lengths for **2d** differ by no more than 0.015 Å from the corresponding experimental bond lengths in the more substituted phospholide derivative.

Compared to the analogous phospholes, the shorter CN bond distances and expanded CNC bond angles in the pyrroles lead to similar CC bond lengths, but smaller CCC bond angles associated with the dienyl moiety, presumably resulting in greater strain in the pyrroles. The change in geometry of **1a** upon deprotonation is far less pronounced than with deprotonation (or planarization) of **2a**. This is due to the fact that the π-conjugation between the lone pair of the planar nitrogen and the dienyl moiety is already substantial, and deprotonation in the σ plane acts mainly to polarize the π-system. The structures computed for the pyrroles **1a–c** in the present study are consistent with earlier calculations at lower levels of theory[42] and with the most recent HF/6-31G(d) calculations by Bachrach.[12] As with the phospholes, the MP2/6-31G(d) geometries for the pyrroles reported by Bachrach exhibit a lesser degree of bond length alternation than do the structures obtained from Hartree–Fock level calculations.

Energetics. *2H*-Phosphole (**2b**) is computed to be the lowest energy C_4H_5P isomer, lying 7.8 kcal/mol below **2a** and 3.8 kcal/mol below **2c** in enthalpy (Table 4). The barrier for the conversion of *1H*-phosphole to *2H*-phosphole by an exothermic 1,5-hydrogen shift has been calculated by Bachrach to be 16.0 kcal/mol.[12] In contrast, the slightly endothermic 1,5-hydrogen shift converting **2b** to **2c** was found to have a barrier of 26.9 kcal/mol, similar to that for rearrangement of d_5-1,3-cyclopentadiene (E_a(c-C_5D_5H, exptl) = 23.6 kcal/mol;[50] E_a(C_5H_6, theory) = 26.4 kcal/mol).[12]

The energy differences among the phosphole and pyrrole tautomers determined in this work are generally in good agreement with the results of the MP2/6-31G(d) calculations by Bachrach,[12] although they are systematically slightly larger for the phospholes and slightly smaller for the pyrroles (Table 4). Higher level MP4SDQ/6-31G(d) calculations of the energy difference between **2a** and **2b** carried out by Bachrach give a slightly higher value of 7 kcal/mol, suggesting that the present values are probably accurate.

The calculated barrier for inversion of the phosphorus in **2a** is 18.9 kcal/mol, compared to the measured[51] $\Delta G^{\ddagger}$(298 K) values of 16 kcal/mol for a 1-phenylphosphole derivative and 36 kcal/mol for an analogous 1-phenylphospholane. The implications of the reduced barrier for **2a** have been discussed previously in terms of the aromaticity of the planar transition state.[2,51]

The phospholes are predicted to be relatively strong Brønsted acids. The computed ΔH_{acid} values for **2a–c** are 333.6, 341.4, and 337.6 kcal/mol, respectively, which ranks them with halogenated carboxylic acids in terms of acid strength.[23] At this same level of theory, the calculated acidity for pyrrole, 358.6 kcal/mol, is in excellent agreement with experiment (359 ± 3 kcal/mol[23]). This suggests that the error in the computed values for the phospholes is not likely to be large.

Discussion

The bracketed proton affinity for the $C_4H_4P^-$ ion of 338 ± 3 kcal/mol is close to the theoretically predicted proton affinities at C-2 (341.4 kcal/mol) and C-3 (337.6 kcal/mol) but is nearly 5 kcal/mol greater than the predicted proton affinity at phosphorus (333.6 kcal/mol). It is noteworthy in this regard that, in solution, protonation and alkylation of phospholide anions have been shown to occur initially at phosphorus.[2,52] However, in the case of protonation, the resulting *1H*-phospholes undergo rapid, irreversible rearrangement to the corresponding *2H* isomers. The preference for kinetic protonation at phosphorus has been discussed in terms of frontier orbital and charge control, since the HOMO of the phospholide anion is localized mainly at phosphorus and the net charge at phosphorus is relatively high.[2]

Since *1H*-phosphole is essentially nonaromatic, the bond energies in the phospholes can be compared to derive the approximate relative stabilities of the *1H*, *2H*, and *3H* structures. In going from the *1H* structure to the *2H* structure, a C=C π bond (typically 65 kcal/mol[53]) and a secondary P–H single bond (*ca.* 70 kcal/mol[54]) are replaced by a C=P π bond (49 kcal/mol[40]) and a secondary C–H single bond (*ca.* 95 kcal/mol[53]). Therefore, although the C=P π bond is weaker by 16 kcal/mol, the C–H single bond is stronger by 25 kcal/mol. The *2H*- and *3H*-phospholes have the same number and type of bonds. Accordingly, both *iso*-phosphole isomers should be more stable than the *1H* isomer by up to about 9 kcal/mol. This is in fact borne out by the calculated total energies, which indicate relative enthalpies for the *1H*, *2H*, and *3H* isomers of 7.8, 0.0, and 4.0 kcal/mol, respectively. This same type of energetic preference for phosphaalkene rather than vinylphosphine structures in acyclic systems has been demonstrated both experimentally[55] and theoretically.[56] The origins of the energetic preference for having phosphorus at the terminal rather than internal positions in a phospha-1,3-butadiene group have been discussed by Bachrach and Liu.[57]

A similar comparison for the arsoles is complicated by the lack of any experimental or theoretical data bearing on the strength of an As=C π bond. The As–H bond in AsH_3 (73.5 ± 3.0 kcal/mol[23]) is 11 kcal/mol weaker than the P–H bond in PH_3 (84.7 ± 0.9 kcal/mol[23]), thus, the energy gained from replacing an As–H bond as in *1H*-arsole with a C–H bond as in the *iso*-arsoles will be even greater than the 25 kcal/mol estimate derived above. On the other hand, an As=C π bond is also likely to be weaker than a P=C π bond because of poor 2p(π)–4p(π) overlap.[58] An As=C π bond strength less than about 29 kcal/mol would make the *1H*-arsole isomer more stable than the *2H* and *3H* isomers.

---

[49] Douglas, T.; Theopold, K. H. *Angew. Chem., Int. Ed.Engl.* **1989**, *28*, 1367.

[50] Roth, W. R. *Tetrahedron Lett.* **1964**, 1009.

[51] (a) Egan, W.; Tang, R.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1970**, *92*, 1442. (b) Egan, W.; Tang, R.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1971**, *93*, 6205.

[52] Charrier, C.; Bonnard, H.; de Lauzon, G.; Mathey, F. *J. Am. Chem. Soc.* **1983**, *105*, 6871 and references therein.

[53] Benson, S. W. *Thermochemical Kinetics*;Wiley: New York, 1976.

[54] Estimated from the reported PH bond energies in PH_3 and CH_3-PH_2, see ref 23 and: Berger, S.; Brauman, J. I. *J. Am. Chem. Soc.* **1992**, *114*, 4737.

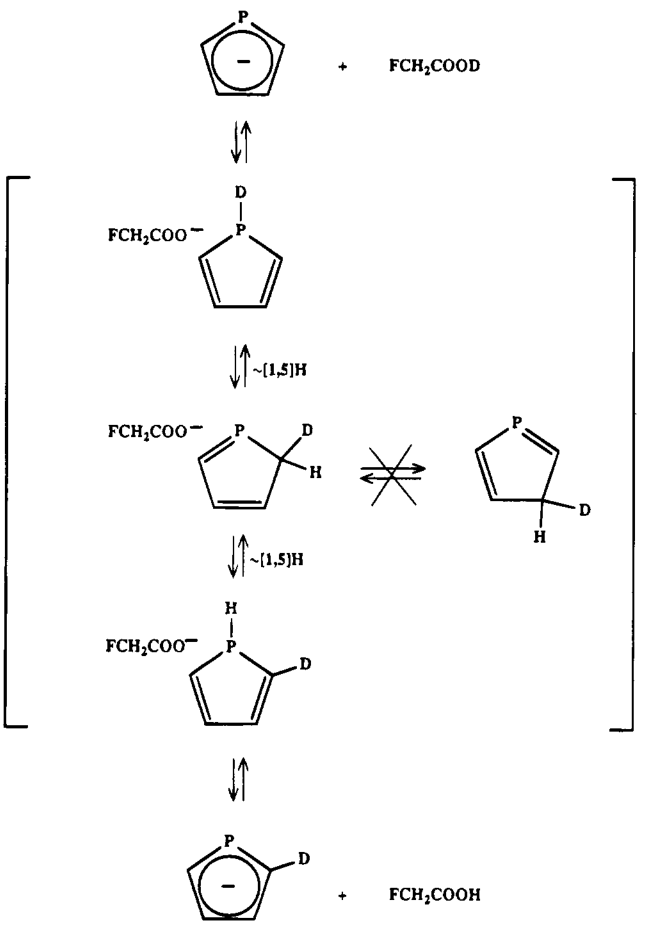
[55] Mercier, F.; Le Goff, C. H.; Mathey, F. *Tetrahedron Lett.* **1989**, *30*, 2397.

[56] Nguyen, M. T.; Landuyt, L.; Vanquickenborne, L. G. *Chem. Phys. Lett.* **1993**, *212*, 543.

[57] Bachrach, S. M.; Liu, M. *J. Am. Chem. Soc.* **1991**, *113*, 7929.

[58] Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272–295.

Scheme 2



The observed H/D exchange behavior of pyrrolide, phospholide, and arsolide anions provides some clues regarding the isomer stability orderings discussed above. No exchange is observed for pyrrolide and arsolide. This indicates that for both systems either the 1*H* isomer is much lower in energy than the other two (a known fact for the pyrrole system) or that carbon protonation is disfavored kinetically (as discussed above for phospholide). Two H/D exchanges are observed for phospholide, indicating that at least one of the carbon protonated forms (probably the 2*H* isomer) is a low energy, kinetically accessible species. In fact, the present calculations suggest that all four hydrogens in $C_4H_4P^-$ should have exchanged, since the 2*H* and 3*H* isomers are relatively close in energy (ΔE < 4 kcal/mol). An unlikely explanation for the fact that only two exchanges could be observed is that the 2*H*/3*H* energy difference is even larger than the theoretical estimate. A more probable scenario, in our view, is that deuteration occurs initially on the phosphorus atom and is followed by slow [1,5] deuterium and hydrogen shifts leading to exchange of the C-2 but not the C-3 hydrogens.[59] A mechanism for this reaction sequence is outlined in Scheme 2. Theoretical calculations[12] give a barrier of 16.0 kcal/mol for the [1,5]-hydrogen migration that converts 1*H*-phosphole to 2*H*-phosphole and a 26.9 kcal/mol barrier for rearrangement of 2*H*-phosphole to 3*H*-phosphole. In the gas phase, such barriers can be overcome by the energy of interaction between the ion and the deuterated acid. For comparison, the energies of solvation of pyrrolide ion by water and methanol are 15.7 and 18.6 kcal/mol, respectively.[31] It is therefore plausible that the phospholide/FCH_2COOD solvation energy is of a sufficient magnitude to overcome the 16 kcal/mol barrier leading to exchange at the C-2 sites but is too low to allow measurable exchange at the C-3 sites. In contrast, the absence of exchange in the arsolide/FCH_2COOD reaction indicates that the 2*H* isomer is not accessed during the ion–molecule encounter, implying that the experimental acidity for arsole most likely corresponds to the 1*H* isomer.

Table 5. Thermochemical Data for Heteroles and Related Compounds[a]

AH	ΔH°_{acid}(AH)	EA(A)	*D*(A–H)
NH_3	403.6 ± 0.8	17.9 ± 0.9	108.9 ± 0.3
PH_3	370.9 ± 2.1	29.3 ± 0.2	84.7 ± 0.9
AsH_3	357.8 ± 2.1	29.3 ± 0.7	73.5 ± 3.0[c]
$H_2C{=}NH$	388.4 ± 5.1	11.8 ± 1.6	87 ± 6[c]
CH_3NH_2	403.3 ± 0.8	10. ± 3[c]	100.0 ± 2.5
$(CH_3)_2NH$	396.5 ± 0.7	9 ± 3[c]	91.5 ± 2.0
pyrrole	359 ± 3	55.1 ± 3.0, ≤52.3[b]	97.0 ± 2.0
phosphole[e]	338 ± 3[b]	≤52.3[b]	≤76.7[c]
arsole[f]	338 ± 3[b]	≤52.3[b]	≤76.7[c]
CH_3PH_2	369 ± 3[d]	21.6 ± 0.4[d]	77 ± 3[c]

[a] All values in kcal/mol. Data from ref 23 unless otherwise noted. [b] This work. [c] Calculated using eq 4. [d] Reference 54. [e] Presumed to correspond to the 2*H* isomer; see text. [f] Presumed to correspond to the 1*H* isomer; see text.

The periodic trends in the acid–base properties of pyrrole, phosphole, and arsole are more complicated than in the corresponding series of simple binary hydrides. The measured acidities (ΔH°_{acid} = 359, 338, and 338 kcal/mol, respectively) do not follow the usual trend of monotonically increasing acidity (decreasing ΔH_{acid}) down a column of the periodic table, *e.g.*, the ΔH_{acid} values for NH_3, PH_3, and AsH_3 are 403.6, 370.9, and 357.8 kcal/mol, respectively.[23] To understand acidity trends, it is often useful to separate ΔH_{acid}(AH) into the components listed in eq 4,[23] where IP(H) = 313.6

$$\Delta H_{acid}(AH) = D(A-H) + IP(H) - EA(A) \qquad (4)$$

kcal/mol is the ionization potential of the hydrogen atom.[60] Thus, a decrease in ΔH_{acid}(AH) can result from a decrease in *D*(A–H) or an increase in EA(A). Relevant data for the present study are given in Table 5. In going from NH_3 to PH_3 and then to AsH_3, ΔH_{acid} drops by 33 and then 13 kcal/mol. Most of this effect is due to the decreases in the A–H bond strength by increments of 24 and 11 kcal/mol, respectively. Also, the electron affinity of PH_2 is higher than that of EA(NH_2) by 11 kcal/mol, although EA(AsH_2) does not increase further.

The large difference between the acidities of NH_3 and pyrrole (45 kcal/mol) can be attributed to several effects. One contribution is the effect of replacing the hydrogens by carbon substituents. For example, ΔH_{acid} for dimethylamine is 7 kcal/mol less than that for ammonia. This effect is largely due to the decrease in N–H bond

---

(59) A conceivable explanation for the occurrence of only two exchanges by the phospholide anion is that the solvation energy in the [$FCH_2COOD\cdots C_4H_4P^-$] complex is just sufficient to allow endothermic deuteration of the C-2 position but not the C-3 position of the ion. However, the absolute energies required for deuteron transfer to either position (0–4 kcal/mol, cf. Table 5) are much less than the estimated total solvation energy of *ca.* 15 kcal/mol;[23] thus, this explanation is unlikely.

(60) For eq 4 to be precise, all values should be at 0 K. Differences between 0 and 298 K can be neglected for the purposes of this work. Also, the values in Table 5 are generally independently measured and may not be in exact accordance with eq 4.

strength (17 kcal/mol), since the electron affinity of $(CH_3)_2N$ is actually 11 kcal/mol less than that of ammonia. Another conceivable contribution is the difference in the hybridization of the nitrogen atom in NH_3 (sp^3) and pyrrole (sp^2). This is difficult to evaluate, due to a lack of suitable models.[61] The main contributor to the difference in acidity between NH_3 and pyrrole is the large increase in electron affinity in going from NH_2 (18 kcal/mol) to pyrrolyl radical (55 kcal/mol). This can be attributed to the reduced electron density at the pyrrolyl radical nitrogen atom compared to NH_2 due to π-conjugation and inductive withdrawal by the vinyl groups.[62]

The difference between the gas-phase acidity of PH_3 and the calculated acidity of *1H*-phosphole is 37 kcal/mol, somewhat less than the value of 45 kcal/mol for the corresponding nitrogen compounds. The hybridizations of phosphine (experimental bond angles 93.7°)[63] and *1H*-phosphole (average PH/PC calculated bond angles 97.7°) are similar, so hybridization makes little or no contribution to the acidity difference. Substituting a single methyl group on phosphine has the same effect on P–H bond strength and electron affinity (and the same lack of effect on acidity) as in the corresponding nitrogen systems.[54] The thermochemistry of dimethylphosphine is not known, but substitution of a second methyl group should cause the P–H bond strength and acidity to drop slightly, as for dimethylamine. The main cause of the enhanced acidity of *1H*-phosphole compared to PH_3 is the large increase in π-conjugation on forming the delocalized phospholide anion. That is, other than dienyl resonance, π-conjugation is negligible for *1H*-phosphole, but it becomes substantial upon deprotonation, leading to an electron affinity for the phospholyl radical that is up to 23 kcal/mol higher than that for PH_2. Although EA(PH_2) is 11 kcal/mol higher than EA(NH_2), EA(C_4H_4P) is less than or equal to EA(C_4H_4N). This suggests that the phosphorus π electrons are less delocalized over the ring and there is less electron withdrawal from the phosphorus atom, so that the electron affinity is less affected.

Interpretation of the arsole acidity is hampered by the dearth of relevant experimental and computational studies involving arsenic compounds. Baldridge and Gordon have performed calculations on *1H*-arsole at the HF/3-21G(d) level[42] that indicate little or no π-conjugation between the arsenic atom and the dienyl moiety, but there are no published studies of arsolide anion. However, structural data for arsine,[64] substituted *1H*-arsoles and transition-metal-coordinated arsolide derivatives[8] show that these arsenic compounds closely resemble their phosphorus analogs. The calculated upper limit to the As–H bond strength in arsole, 77 kcal/mol, is very high. It is likely that the actual value is significantly less than this limit. This would mean that EA(C_4H_4As) must be correspondingly lower than the indicated limit of 52 kcal/mol. The 20 kcal/mol difference between the acidities of *1H*-arsole and AsH_3 is much smaller than the corresponding values for the nitrogen and phosphorus analogs (37–45 kcal/mol). The smaller acidity difference suggests a smaller delocalization energy for arsolide than for phospholide, in accord with the suspected lower electron affinity of C_4H_4As. This is consistent with the weaker π-bonding in arsabenzene compared to phosphabenzene.[65]

Summary

The bracketed proton affinities for phospholide and arsolide anions are found to be the same at 338 ± 3 kcal/mol. The occurrence of H/D exchange for the phospholide ion and the theoretical results suggest that the *2H*-phosphole isomer plays an important role in the gas phase acid–base chemistry of phospholide anion. The absence of H/D exchange with the arsolide and pyrrolide anions is indicative of exclusive heteroatom protonation without intercession of the corresponding *iso*-heteroles. The $C_4H_4X^-$ (X = N, P, As) ions are relatively unreactive in the gas phase, showing only addition or clustering reactions with polar or electrophilic neutral molecules, and electron transfer with NO_2. Molecular orbital calculations predict *2H*-phosphole to be the most stable C_4H_5P isomer and give proton affinities for the P, C-2, and C-3 positions of phospholide anion of 333.6, 341.4, and 337.6 kcal/mol, respectively. The activation energy for phosphorus inversion in the nonaromatic *1H*-phosphole isomer is predicted to be 18.9 kcal/mol. The aromatic *1H*-pyrrole is the most stable C_4H_5N isomer, and the proton affinities at N, C-2, and C-3 of the pyrrolide anion are predicted to be 358.6, 347.1, and 345.6 kcal/mol, respectively.

Acknowledgment. This work was funded by the National Science Foundation and the Department of Energy, Office of Basic Energy Science. We thank Professor S. Bachrach for helpful discussions and Dr. E. H. Borneman for synthesizing the sample of CF_3CH_2OD in 1952.

OM940517H

---

[61] The difference in the acidities of $H_2C{=}NH$ (sp^2 N) and H_3C-NH_2 (sp^3 N) is 15 kcal/mol. However, this difference is mainly due to the 13 kcal/mol weaker N–H bond strength in the former, which results from the large nitrogen valence promotion energy in the radical $H_2C{=}N$. These effects are absent in the pyrrole system.

[62] Barton, T. J.; Roth, R. W.; Verkade, J. G. *J. Am. Chem. Soc.* **1972**, *94*, 8854 and references cited therein.

[63] Fluck, E. *Top. Curr. Chem.* **1973**, *35*, 1.

[64] Blevis, G. S.; Jache, A. W.; Gordy, W. *Phys. Rev.* **1955**, *97*, 685.

[65] (a) Ashe, A. J., III; *Acc. Chem. Res.* **1978**, *11*, 153. (b) Ashe, A. J., III; Gordon, M. D. *J. Am. Chem. Soc.* **1972**, *94*, 7596.