HC≡P and $H_3C-C{\equiv}P$ as Proton Acceptors in Protonated Complexes Containing Two Phosphorus Bases: Structures, Binding Energies, and Spin−Spin Coupling Constants

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Ab initio calculations at the MP2/aug'-cc-pVTZ level have been carried out to investigate the structures and binding energies of cationic complexes involving protonated sp, sp^2, and sp^3 phosphorus bases as proton donor ions and the sp-hybridized phosphorus bases H−C≡P and $H_3C-C{\equiv}P$ as proton acceptors. These proton-bound complexes exhibit a variety of structural motifs, but all are stabilized by interactions that occur through the π cloud of the acceptor base. The binding energies of these complexes range from 6 to 15 kcal/mol. Corresponding complexes with $H_3C-C{\equiv}P$ as the proton acceptor are more stable than those with H−C≡P as the acceptor, a reflection of the greater basicity of $H_3C-C{\equiv}P$. In most complexes with sp^2- or sp^3-hybridized P−H donor ions, the P−H bond lengthens and the P−H stretching frequency is red-shifted relative to the corresponding monomers. Complex formation also leads to a lengthening of the C≡P bond and a red shift of the C≡P stretching vibration. The two-bond coupling constants ${}^{2\pi h}J(P-P)$ and ${}^{2\pi h}J(P-C)$ are significantly smaller than ${}^{2h}J(P-P)$ and ${}^{2h}J(P-C)$ for complexes in which hydrogen bonding occurs through lone pairs of electrons on P or C. This reflects the absence of significant s electron density in the hydrogen-bonding regions of these π complexes.

Introduction

The relatively simple phosphorus-containing triply bonded molecules investigated in this study, namely, methylidynephosphine (methinophosphide, phosphaethyne, or phosphacetylene) H−C≡P, and ethylidynephosphine $H_3C-C{\equiv}P$, are important because of their potential functionality, although the most chemically used derivative is t-$C_4H_9-C{\equiv}P$ [2,2-dimethylpropylidyne)phosphine]. However, theoretical studies of the parent molecule HCP are numerous. In recent years these have included CCSD(T) calculations of its nuclear spin-rotation coupling constants,[1] and high-level ab initio [CCSD(T), CBS-QB3, CASSCF, CASPT2, MR-ACPF, MR-ACPF-2] and density functional theory (B3LYP) calculations carried out to study the 2 + 2 dimerization of HCP.[2] The singlet ground and excited states of HCP and HPC have also been systematically investigated by high-level ab initio molecular electronic structure methods,[3] and the molecular size of HCP has been evaluated.[4] Finally, information about the synthesis[5] and NMR spectroscopic properties of these and related systems, isolated or coordinated to metals, has been published.[1,6−10]

In a previous paper, we reported the structures, binding energies, and spin−spin coupling constants for a series of cationic complexes formed from bases with sp^2- and/or sp^3-hybridized P atoms and stabilized by $P-H^+\cdots P$ hydrogen bonds.[11] For these complexes, double minima are found along the proton-transfer coordinate when the protonation energies of the two hydrogen-bonded bases differ by less than 16 kcal/mol. The isomer in which the stronger base is protonated lies lower on the potential surface, but the isomer in which the weaker base is protonated has the greater binding energy relative to the corresponding isolated monomers. All of these complexes are stabilized by traditional hydrogen bonds, as indicated by both structural data and one-bond ${}^1J(P-H)$ and ${}^{1h}J(H-P)$, and two-bond ${}^{2h}J(P-P)$ spin−spin coupling constants. ${}^1J(P-H)$ always increases relative to the isolated monomer, while ${}^{1h}J(H-P)$ is relatively small and negative. For open complexes, ${}^{2h}J(P-P)$ values are quite large and correlate with the P−P distance.

Notably absent from that study are complexes with sp-hybridized phosphorus bases. These bases are relatively weak and are not protonated in the presence of the stronger sp^2 and sp^3 bases. Moreover, protonation of H−C≡P does not occur at P but at the π system near the C end of the C≡P bond, forming a nonclassical cation.[12] The question that naturally arises is what type of complexes will sp-hybridized bases like H−C≡P and $H_3C-C{\equiv}P$ form in the presence of a protonated phosphorus base. To address this question we have extended our previous studies of cationic complexes to two series in which H−C≡P and $H_3C-C{\equiv}P$ are the proton acceptor molecules and the conjugate acids of sp, sp^2, or sp^3 phosphorus bases are the proton donor ions. These complexes are identified by number in Scheme 1.

Methods

The structures of all complexes were fully optimized at second-order Møller-Plesset perturbation theory (MP2)[13−16] with the Dunning aug'-cc-pVTZ basis set,[17,18] which has the aug-cc-pVTZ basis on C and P atoms and the cc-pVTZ basis on H. Vibrational frequencies were computed to establish that the optimized structures are local minima on the potential surfaces.

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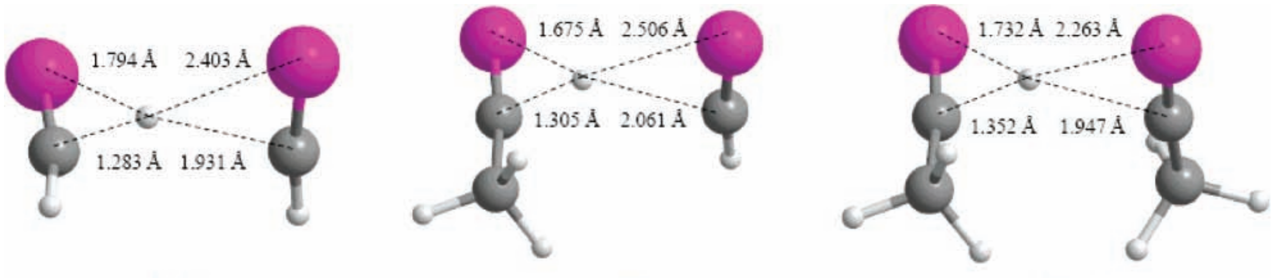


1 (C_1) **2** (C_1) **7** (C_1)

Figure 1. Geometries of complexes **1**, **2**, and **7**.

SCHEME 1

	sp		sp^2		sp^3	
	$[H{-}C{\equiv}P]H^+$	$[H_3C{-}C{\equiv}P]H^+$	$[H{-}P{=}\underset{H}{P}{-}H]^+$	$[H{-}\underset{H}{C}{=}\underset{H}{P}{-}H]^+$	$H{-}\overset{H}{\underset{H}{P^+}}{-}H$	$H_3C{-}\overset{H}{\underset{H}{P^+}}{-}H$
$H{-}C{\equiv}P$	1	2	3	4	5	6
$H_3C{-}C{\equiv}P$	goes to **2**	7	8	9	10	11

The transition structures for proton transfer have also been found for the protonated homodimers $(HCP)_2H^+$ and $(H_3CCP)_2H^+$.

Due to the size of these complexes and their low symmetries, spin−spin coupling constants were computed only for complex **1** (C_1 symmetry) and complexes **3**, **4**, and **5** with HCP as the proton acceptor and complex **10** with H_3CCP as the proton acceptor (all with C_s symmetry). Coupling constants were evaluated by the equation-of-motion coupled-cluster singles and doubles method (EOM-CCSD) in the CI (configuration interaction) -like approximation[19−22] with all electrons correlated. The Ahlrichs[23] qzp basis was used on C, qz2p on P and the H atom or atoms of the donor ion that interact with the proton acceptor molecule, and the cc-pVDZ basis on all other hydrogens. The total spin−spin coupling constant is a sum of four terms, namely, the paramagnetic spin−orbit (PSO), diamagnetic spin−orbit (DSO), Fermi contact (FC), and spin−dipole (SD).[24] Only FC terms were evaluated and used to approximate total coupling constants (J), except for complex **1**. That the FC term approximates J quite well for coupling across $P{-}H^+{\cdots}P$ hydrogen bonds was demonstrated in ref 11, and its ability to approximate J for P−H and C−H couplings and intermolecular couplings in the π complexes will be further examined below.

The optimization and frequency calculations were done with Gaussian 03[25] on the computing facilities at the Centro Técnico de Informática (CSIC). The coupling constant calculations were carried out with ACES II[26] on the Itanium cluster at the Ohio Supercomputer Center.

Results and Discussion

A total of 11 cationic complexes were investigated in which neutral HCP or H_3CCP are the proton acceptor molecules. These include three proton-bound complexes containing the two protonated sp-hybridized P bases as donor ions, and eight complexes in which protonated sp^2 bases ($HPPH_2^+$ and $H_2CPH_2^+$) or sp^3 bases (PH_4^+ and $H_3CPH_3^+$) are the donors. As noted above, HCP and H_3CCP are not protonated in the presence of sp^2 or sp^3 P bases. The complex formed from protonated HCP as the donor ion to H_3CCP is not stable but spontaneously evolves to complex **2**. Selected intermolecular distances are illustrated in Figures 1−3. The full geometries of the equilibrium structures are included as Supporting Information.

Structures of Complexes Involving Two sp P Bases. In contrast to the structures of complexes stabilized by linear $P{-}H^+{\cdots}P$ hydrogen bonds formed between sp^2- and/or sp^3-hybridized phosphorus bases,[11] different structural motifs are evident in Figure 1 for complexes **1**, **2**, and **7**, which are proton-bound complexes containing two sp-hybridized P bases. Since the hydrogen bonds in the protonated homodimers **1** and **7** are not symmetric, the corresponding potential surfaces have two equivalent minima. In these complexes and in complex **2**, in which $(H_3CCP)H^+$ is the proton donor to HCP, the hydrogen-bonded proton lies near the center of the donor π cloud, rather than at the C end of the C≡P bond as it does in the isolated ion. Hydrogen-bond formation with the proton acceptor molecule also occurs near the center of its π cloud. Thus, the structures of these complexes may be described as proton-bound π complexes.

For the two complexes in which the protonated proton donor and proton acceptor bases are identical (**1** and **7**), equivalent double minima exist along the proton-transfer coordinate. The transition states (TS) connecting these minima have been located, and the computed barriers to proton transfer are only 0.5 kcal/mol, as reported in Figure 2. These small barriers imply that the potential surfaces are quite flat in this region so that the proton can easily move from one minimum to the other. The TS structures have C_2 symmetry, with short intermolecular distances relative to the equilibrium structures, a common feature along proton-transfer coordinates. As expected, the centers of the two triple bonds are almost perfectly aligned with the proton in the TS structures.

Structures of Complexes with sp^2 and sp^3 Protonated Phosphorus Bases as Proton Donor Ions. Since the two sp-hybridized P bases HCP and H_3CCP are not protonated in the presence of an sp^2 or sp^3 P base, the sp bases are always the proton acceptor molecules in cationic complexes, and only a single minimum is found along the proton-transfer coordinate. The optimized structures of all of the complexes formed between

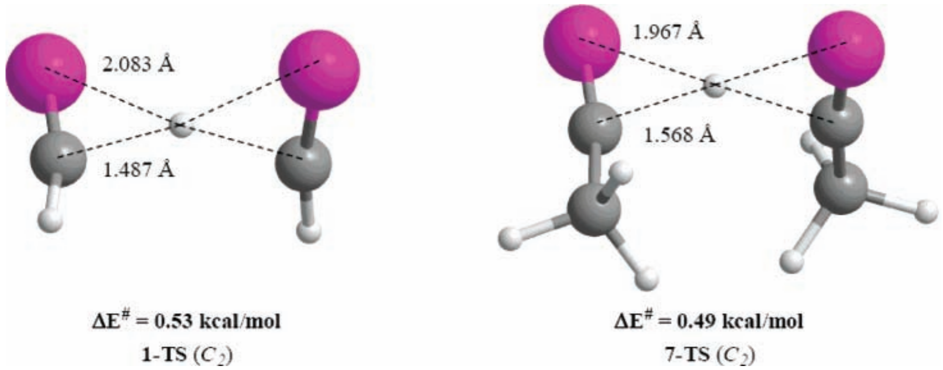


Figure 2. Geometries of TS structures and barriers to proton transfer for complexes **1** and **7**.

the protonated sp^2 and sp^3 bases as donor ions and HCP and H_3CCP as acceptors are illustrated in Figure 3. It is apparent from Figure 3 that the structures of the pair of complexes that have the same proton donor ion to the two sp bases are similar. For example, complexes **3** and **8**, in which $HP{=}PH_2^+$ is the proton donor to HCP and H_3CCP, are cyclic and stabilized by $P-H^+\cdots C$ and $P-H\cdots P$ interactions through the π clouds of the proton acceptor molecules. The H···C distance is significantly shorter than the H···P distance in these complexes, most probably due to several factors including (1) the $P-H^+\cdots C$ interaction is stronger since it involves the protonated P−H group; (2) the π cloud of the base is polarized toward the C end of the C≡P bond; and (3) the van der Waals radius of C is shorter than that of P. In addition, corresponding H···C and H···P distances in the complex with H_3CCP are slightly shorter than those in the complex with HCP, suggesting that the former is more tightly bound.

Complexes **4** and **9**, in which $H_2C{=}PH_2^+$ is the proton donor, and complexes **5** and **10**, in which PH_4^+ is the proton donor, have similar structures insofar as a single $P-H^+$ group interacts with the π cloud of the acceptor C≡P bond. Corresponding H···C and H···P distances in the complexes with H_3CCP are significantly shorter. Complexes **5** and **10** have C_s symmetry. In contrast, while complex **4** has a planar C_s structure, complex **9** has C_1 symmetry with the donor ion and the acceptor base in nearly perpendicular planes. However, because the planar and perpendicular structures can be interconverted by a simple rotation about the donor $P-H^+$ bond, the energy difference between the two orientations is less than 0.5 kcal/mol. The remaining pair of complexes (**6** and **11**) have $H_3CPH_3^+$ as the proton donor ion to the two bases. In these complexes of C_1 symmetry, two P−H bonds and one C−H bond of the donor straddle the C≡P π clouds of HCP and H_3CCP, as illustrated in Figure 3.

The calculated π-complexes can be considered analogous to those obtained between acetylene with both neutral and charged hydrogen-bonding donors.[27−29] In addition, they show a similar structure to the reported platinum complexes of ethylidynephosphine, which correspond to dihapto complexes.[10]

Interaction Energies. Table 1 reports the binding energies of the complexes with HC≡P and $H_3CC{\equiv}P$ as the proton acceptor molecules. From these data it can be seen that for the series of complexes with HCP as the proton acceptor, the largest binding energy is found for the complex in which protonated HCP is the donor ion, forming the protonated homodimer $(HCP)_2H^+$ **1**. Similarly, the protonated dimer of $(H_3CCP)_2H^+$ **7** also has the largest binding energy in the series of complexes with H_3CCP as the proton acceptor. Since HCP and H_3CCP are the weakest bases, $(HCP)H^+$ and $(H_3CCP)H^+$ are the strongest conjugate acids, and hence the best proton-donor ions for hydrogen-bond formation.

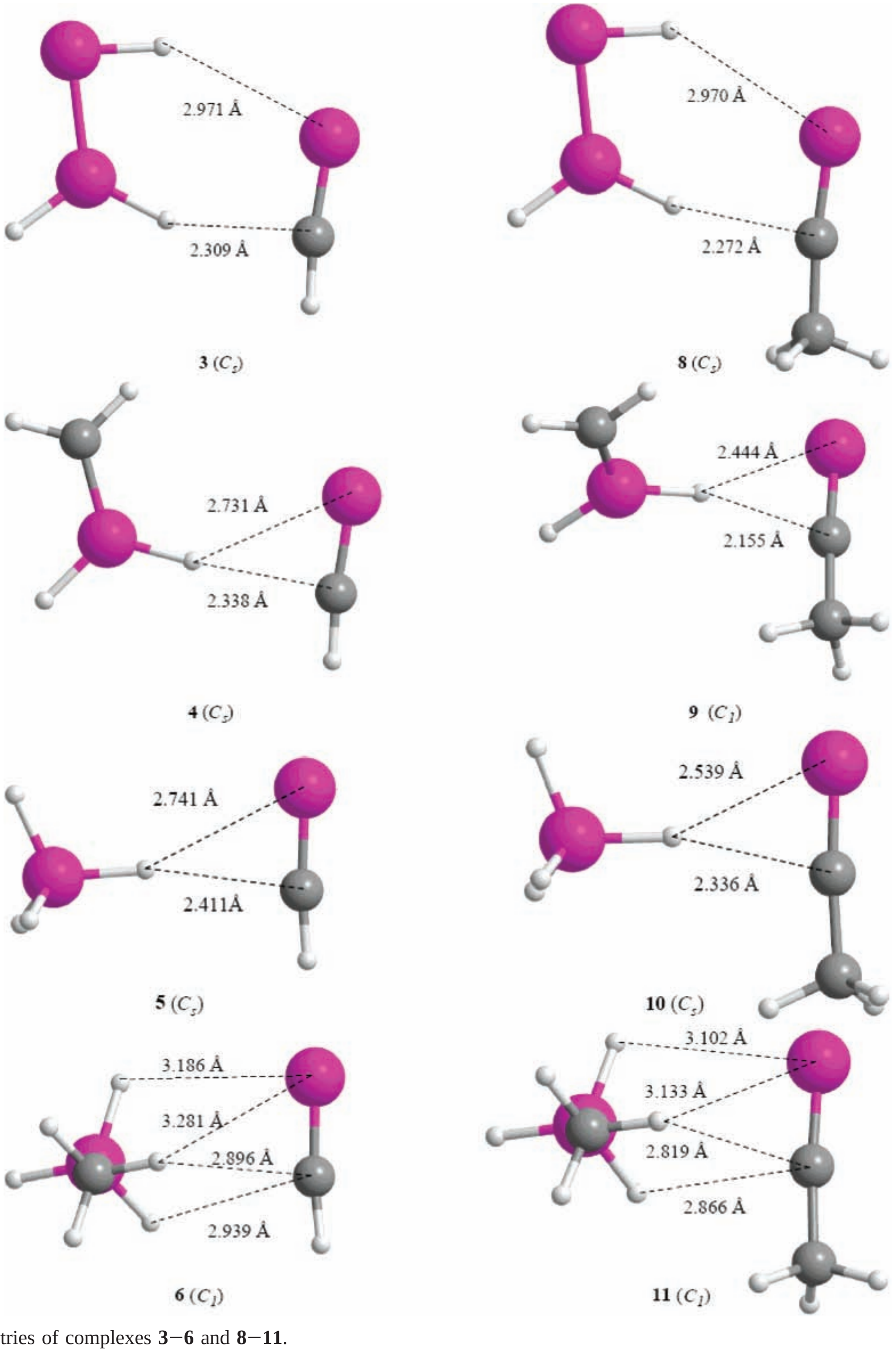
From Table 1 it can be seen that the binding energies of these complexes tend to decrease as the hybridization of P in the proton-donor ion changes from sp to sp^2 to sp^3. As judged by their computed protonation energies (PE), the weakest bases are the sp bases (HCP and H_3CCP; PE = 161 and 170 kcal/mol, respectively), followed by the sp^2 bases (H_2CPH, *cis*-HPPH, and *trans*-HPPH; PE = 184, 186, and 183 kcal/mol, respectively), and then the sp^3 bases (PH_3 and H_3CPH_2; PE = 193 and 209 kcal/mol, respectively). Thus, the order of decreasing binding energies is determined primarily by the order of increasing base strength of the base that is protonated, that is, the order of decreasing strength of the conjugate acid that is the proton donor. It should be noted, however, that corresponding complexes with $HPPH_2^+$ as the donor ion are more stable than those with $H_2CPH_2^+$, a result of the cyclic nature of the former complexes, which are stabilized by $P-H^+\cdots\pi$ and $P-H\cdots\pi$ interactions. Moreover, it may also be that the structural differences between complexes with PH_4^+ and $H_3CPH_3^+$ are responsible for the greater stabilities of the complexes with $H_3CPH_3^+$.

It is also apparent from Table 1 that for a given proton-donor ion, the complex formed with the stronger base H_3CCP always has a greater binding energy than the corresponding complex with HCP. A linear relationship between the binding energies of pairs of these complexes with the same proton donor is given as

$$-\Delta E_e(H_3CCP) = 1.2994\,[-\Delta E_e(HCP)] + 0.6095 \qquad R^2 = 0.99,\ n = 5 \quad (1)$$

where $-\Delta E_e(H_3CCP)$ is the electronic binding energy of the complex with H_3CCP as the proton acceptor and $-\Delta E_e(HCP)$ is the electronic binding energy of the complex with the same proton donor and HCP as the proton acceptor. It is also interesting to note that the binding energies of the complexes investigated in this study are comparable to the binding energies for complexes with $P-H^+-P$ hydrogen bonds in which hydrogen bonding occurs through a lone pair of electrons on sp^2 or sp^3 P atoms.[11]

Harmonic Frequencies. Table 2 presents the P−H distances and harmonic P−H stretching frequencies for the isolated sp^2 and sp^3 donor ions and for complexes of these ions with HCP and H_3CCP. In complexes with $HPPH_2^+$ as the donor, the P−H bond of the PH_2^+ group lengthens by 0.013 and 0.022 Å in the complexes with HCP and H_3CCP, respectively, and the corresponding P−H stretching vibrations are red-shifted by 141 and 234 cm^{-1}. A similar but smaller effect is found for changes in the P−H distance and stretching frequency of the interacting



3 (C_s) **8** (C_s) **4** (C_s) **9** (C_1) **5** (C_s) **10** (C_s) **6** (C_1) **11** (C_1)

Figure 3. Geometries of complexes **3**−**6** and **8**−**11**.

nonprotonated P−H, which experiences a lengthening of the bond by only 0.006 Å in both complexes, and smaller red shifts of 53 and 54 cm^{-1} in complexes with HCP and H$_3$CCP, respectively. The maximum change in the P−H distance and P−H stretching frequency among these complexes occurs when H$_2$CPH$_2^+$ is the donor ion to H$_3$CCP. For this complex, the P−H bond stretches by 0.042 Å, and the P−H stretching frequency is red-shifted by 510 cm^{-1}. In contrast, in the complex formed between H$_2$CPH$_2^+$ and HCP, the P−H bond of the donor lengthens by only 0.010 Å, and the red shift of the stretching vibration is only 204 cm^{-1}. When PH$_4^+$ is the proton donor, the lengthening of the P−H bond and the red shift of the P−H

TABLE 1: Binding Energies of Complexes

no.	donor	acceptor	$-\Delta E_e$ (kcal mol^{-1})
1	HCPH$^+$	HCP	11.64
2	H$_3$CCPH$^+$	HCP	10.85
3	HPPH$_2^+$	HCP	7.38
4	H$_2$CPH$_2^+$	HCP	6.93
5	PH$_4^+$	HCP	6.26
6	H$_3$CPH$_3^+$	HCP	6.97
7	H$_3$CCPH$^+$	H$_3$CCP	14.68
8	HPPH$_2^+$	H$_3$CCP	10.25
9	H$_2$CPH$_2^+$	H$_3$CCP	10.01
10	PH$_4^+$	H$_3$CCP	8.60
11	H$_3$CPH$_3^+$	H$_3$CCP	9.39

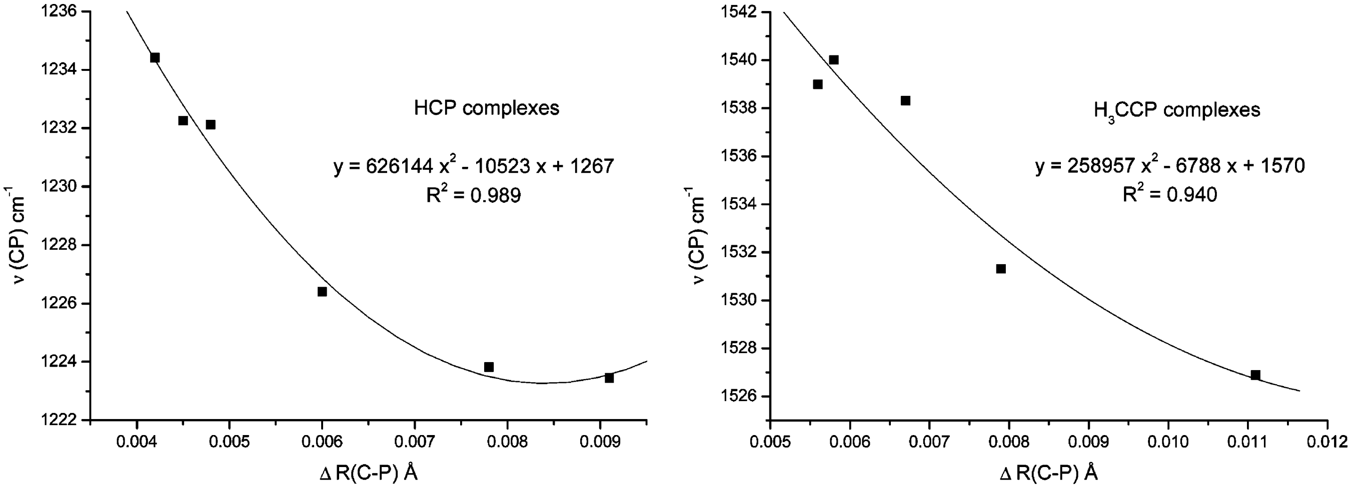


Figure 4. C≡P stretching frequency versus change in the C≡P distance for complexes with HCP and H_3CCP.

TABLE 2: Harmonic P−H Stretching Frequencies of Proton Donors, P−H Distances, and Lengthening of the P−H Bonds for Complexes with sp^2- and sp^3-hybridized P−H Donors

	ν (cm^{-1})			R(P−H), Å			ΔR(P−H), Å	
donor	isolated	complexes with HCP	complexes with H_3CCP	isolated	complexes with HCP	complexes with H_3CCP	complexes with HCP	complexes with H_3CCP
$HPPH_2^+$	2437 (PH)	2384	2383	1.421	1.427	1.427	0.006	0.006
$HPPH_2^+$	2548 (PH_2)	2407	2314	1.397	1.410	1.419	0.013	0.022
$H_2CPH_2^+$	2642	2438	2132	1.391	1.401	1.433	0.010	0.042
PH_4^+	2627	2407	2301	1.392	1.409	1.418	0.016	0.026
$H_3CPH_3^+$	2616	2614, 2629	2614, 2631	1.394	1.392	1.391	−0.002[a]	−0.002[a]

[a] Average of the two interacting P−H bonds of the donor ion.

stretching frequency are again greater when H_3CCP is the acceptor ($\Delta R = 0.026$ Å and $\Delta\nu = 326$ cm^{-1}) compared to HCP ($\Delta R = 0.016$ Å and $\Delta\nu = 220$ cm^{-1}). Finally, the complexes in which $H_3CPH_3^+$ is the donor exhibit only small changes in P−H distances and stretching frequencies. These small changes most probably reflect the unique structure of this complex in which the donor ion straddles the π cloud of the acceptor, giving rise to long intermolecular H···P and H···C distances and only a small perturbation of the P−H bonds.

Since hydrogen-bond formation perturbs the π clouds of HCP and H_3CCP, it may be anticipated that the π bonds should be weaker in the complexes than in the isolated monomers. The weakening of the C≡P π bond results in a lengthening of this bond and a decrease in the C≡P harmonic stretching frequency. A quadratic relationship between changes in C≡P distances and red shifts of C≡P stretching frequencies is illustrated in Figure 4 for complexes with HCP and H_3CCP. The second-order curves shown have correlation coefficients of 0.989 and 0.940, respectively.

Spin−Spin Coupling Constants. It is customary to designate couplings across X−H···Y hydrogen bonds as ${}^1J$(X−H), ${}^{1h}J$(H−Y), and ${}^{2h}J$(X−Y). However, in the proton-bound complexes investigated in this study, Y may not be unambiguously defined since hydrogen bonding occurs through the π system, often near the midpoint of the C≡P bond. In complexes **1**, **2**, and **7**, X is not unambiguously defined as well. Therefore, for these complexes we propose the new designations ${}^{1\pi h}J$(H−Y) and ${}^{2\pi h}J$(X−Y) as a reminder of the distinctive nature of the couplings in these hydrogen-bonded π complexes. For complexes **1**, **2**, and **7** we propose ${}^{1\pi}J$(X−H) for X−H coupling in the donor ion.

Total spin−spin coupling constants for complex **5** and the contributions of the individual terms that contribute to J are reported in Table 3. Complex **5** is stabilized by one P−H⁺···π hydrogen bond, and one- and two-bond coupling constants are reported for both P−H⁺···P and P−H⁺···C interactions. As evident from Table 3, the FC terms dominate and approximate the one-bond coupling constant ${}^1J$(P−H) and the two-bond coupling constants ${}^{2\pi h}J$(P−P) and ${}^{2\pi h}J$(P−C) quite well. Corresponding FC terms for the one-bond coupling across the hydrogen bond also approximate ${}^{1\pi h}J$(H−P) and ${}^{1\pi h}J$(H−C) well, although these couplings are quite small, and the FC term approximates J due to a cancellation effect of the other terms. Nevertheless, the FC terms are good approximations and will be used below to approximate J.

TABLE 3: Spin−Spin Coupling Constants and Their Components for Complex 5 (PH_4^+:HCP)[a]

	PSO (Hz)	DSO (Hz)	FC (Hz)	SD (Hz)	J (Hz)
	P−H⁺···P Coupling across π Hydrogen Bond				
${}^{2\pi h}J$(P−P)	−0.2	0.0	21.5	2.1	23.4
${}^1J$(P−H)	0.2	0.2	526.3	0.2	526.9
${}^{1\pi h}J$(H−P)	−2.0	0.5	−3.1	1.0	−3.6
	P-H⁺···C Coupling across π Hydrogen Bond				
${}^{2\pi h}J$(P−C)	0.0	0.0	6.8	0.3	7.2
${}^1J$(P−H)	0.2	0.2	526.3	0.2	526.9
${}^{1\pi h}J$(H−C)	−0.4	0.6	−1.3	−0.2	−1.3

[a] The total spin−spin coupling constant J is a sum of four terms: paramagnetic spin−orbit (PSO), diamagnetic spin−orbit (DSO), Fermi contact (FC), and spin−dipole (SD).

The complexes with sp bases as proton acceptors are stabilized by hydrogen bonds that form through the C≡P triple bonds of H−C≡P and H_3C−C≡P. As evident from Figure 1, the hydrogen-bonded proton in complex **1** is positioned near the midpoint of the C≡P bonds of the two HCP molecules. Table 4 reports Fermi-contact terms (referred to below as coupling constants J) for P−H⁺···P, P−H⁺···C, and C−H⁺···C interactions. Not surprisingly, the three two-bond coupling constants ${}^{2\pi h}J$(P−P), ${}^{2\pi h}J$(P−C), and ${}^{2\pi h}J$(C−C) are

TABLE 4: Fermi Contact Terms across π Hydrogen Bonds for Complexes 1, 3, 4, and 10 and Corresponding Donor Ions

complex	FC terms[a] (Hz)	$P-H^+\cdots P(\pi)$	$P-H^+\cdots C(\pi)$	$C-H^+\cdots C(\pi)$
1[b]	${}^{2\pi h}J(X-Y)$	4.0 (6.4)	1.5 (3.9)	1.7 (5.5)
1[b]	${}^{1\pi}J(X-H)$	−26.2 (−6.1)	−26.2(−6.1)	38.3 (18.5)
1[b]	${}^{1\pi h}J(H-Y)$	−7.7 (−6.1)	−3.1(18.5)	−3.1 (18.5)
3	${}^{2\pi h}J(X-Y)$	3.0	9.2	
3	${}^{1}J(X-H)$	136.2	594.5	
3	${}^{1\pi h}J(H-Y)$	−6.1	−1.6	
4	${}^{2\pi h}J(X-Y)$	25.3	9.6	
4	${}^{1}J(X-H)$	663.0	663.0	
4	${}^{1\pi h}J(H-Y)$	−3.0	−1.6	
10	${}^{2\pi h}J(X-Y)$	38.7	8.6	
10	${}^{1}J(X-H)$	526.7	526.7	
10	${}^{1\pi h}J(H-Y)$	−5.8	−1.8	

	donor ion	X−H	${}^{1\pi}J(X-H)$; ${}^{1}J(X-H)$[a]
1	$(HCP)H^+$	P−H	−39.7
1		C−H	49.5
3	$HPPH_2^+$	P−H[c]	561.1
3		P−H	141.3
4	$H_2CPH_2^+$	P−H	637.2
5, 10	PH_4^+	P−H	499.3

[a] Total coupling constants are approximated by the FC terms. [b] Values for the C_2 transition structures are given in parentheses. [c] Protonated P.

very small, ranging from 1.5 to 4.0 Hz. Although it is possible to define a one-bond coupling constant ${}^{1\pi}J$(P−H) in isolated $(HCP)H^+$, it should be recognized that H^+ is not bonded to P but is displaced toward the C end of the π bond. This may account in part for the negative value of ${}^{1\pi}J$(P−H). The absolute value of this coupling constant then decreases from −39.7 Hz in the ion to −26.2 Hz in complex **1**. Similarly, the C−H coupling constant ${}^{1\pi}J$(C−H) also decreases upon complexation from 49.5 to 38.3 Hz. The one-bond coupling constants ${}^{1\pi h}J$(H−P) and ${}^{1\pi h}J$(H−C) are −7.7 and −3.1 Hz, respectively.

The data in parentheses in Table 4 are coupling constants computed for the C_2 transition structure of **1**. The two-bond coupling constants ${}^{2\pi h}J$(P−P), ${}^{2\pi h}J$(P−C), and ${}^{2\pi h}J$(C−C) increase when the hydrogen bond is symmetric, as they do for complexes with symmetric hydrogen bonds formed through lone pairs of electrons.[11] In part, this is a consequence of the shorter distances associated with symmetric, proton-shared hydrogen bonds.[30] The one-bond coupling constants ${}^{1\pi}J$(P−H) and ${}^{1\pi}J$(C−H) decrease in absolute value, as expected. However, for the symmetric structure ${}^{1\pi}J$(C−H) and ${}^{1\pi h}J$(H−C) are equal and positive, while ${}^{1\pi}J$(P−H) and ${}^{1\pi h}J$(H−P) are equal and negative. A negative value for this one-bond P−H coupling constant is quite unusual[31] and most probably reflects the fact that H^+ is not really bonded to P in the isolated ion $(HCP)H^+$ or in the complexes. It should also be noted that since the magnetogyric ratios of ${}^{1}H$, ${}^{13}C$, and ${}^{31}P$ are positive, the signs of the coupling constants J and the corresponding reduced coupling constants K are the same.

Complex **3** has a cyclic structure, and it and complex **8** are the only complexes stabilized by two different π interactions, one $P-H^+\cdots C$ and the other $P-H\cdots P$. Both two-bond coupling constants ${}^{2\pi h}J$(P−C) and ${}^{2\pi h}J$(P−P) are small and positive, with ${}^{2\pi h}J$(P−C) equal to 9.2 Hz at a P−C distance of 3.662 Å and ${}^{2\pi h}J$(P−P) equal to 3.0 Hz at a P−P distance of 4.255 Å. There is also a third two-bond coupling constant ${}^{2\pi h}J$(P−P) involving the donor $P-H^+$ and the acceptor P, which has a value of 17.7 Hz at a shorter P−P distance of 3.866 Å. Both one-bond coupling constants ${}^{1}J$(P−H) are positive, although ${}^{1}J$(P−H) for the $P-H^+$ donor increases upon complexation, while ${}^{1}J$(P−H) for the neutral donor decreases. Both ${}^{1\pi h}J$(H−P) and ${}^{1\pi h}J$(H−C) are small and negative.

Complexes **4**, **5**, and **10** have a single $P-H^+$ bond involved in hydrogen bonding with the π system of HCP or H_3CCP. As evident from Tables 3 and 4, ${}^{2\pi h}J$(P−P) values for these three complexes are much larger than for complexes **1** and **3**, ranging from 22 to 39 Hz. However, these coupling constants are extremely small relative to those found for complexes with linear $P-H^+\cdots P$ hydrogen bonds formed through a lone pair of electrons on the base, for which ${}^{2h}J$(P−P) values are in the range of several hundred hertz.[11] ${}^{2\pi h}J$(P−C) values in these complexes range from 7 to 10 Hz and are comparable to the value for complex **3** (9.2 Hz). ${}^{1}J$(P−H) always increases in complexes **4**, **5**, and **10** relative to the corresponding isolated monomers, and ${}^{1\pi h}J$(H−P) and ${}^{1\pi h}J$(H−C) are negative. ${}^{2\pi h}J$(P−P) and ${}^{2\pi h}J$(P−C) for complexes **5** and **10**, which have the same proton donor but different acceptors, are 21.5 and 6.8 Hz, respectively, for **5** and 38.7 and 8.6 Hz, respectively, for **10.** The larger values for **10** most probably reflect the shorter P−P and P−C distances, a consequence of the increased base strength of H_3CCP compared to HCP.

The two-bond spin−spin coupling constants ${}^{2\pi h}J$(P−P) in the proton-bound π complexes are much smaller than ${}^{2h}J$(P−P) in complexes in which hydrogen-bond formation occurs through a lone pair of electrons on P. ${}^{2h}J$(P−P) values in such complexes with open structures and essentially linear hydrogen bonds are large and positive, varying from 245 Hz in a complex with $H_3CPH_3^+$ as the proton donor to P_2H_2 (*trans*) to 765 Hz in a complex with $HPPH_2^+$ as the donor to PH_3.[11] In the cyclic complexes with distorted nonlinear hydrogen bonds, values of ${}^{2h}J$(P−P) are reduced but still range from 161 to 329 Hz across $P-H^+-P$ hydrogen bonds. Why are these coupling constants for the π complexes with sp-hybridized bases so small relative to those of complexes with sp^2 and sp^3 bases? While there are a variety of explanations that might be given, two are considered here.

(1) The hydrogen bonds formed with sp bases have π electrons as proton acceptors, but the FC term that dominates ${}^{2\pi h}J$(P−P) is a contact term that depends on ground and excited triplet-state s electron densities at the coupled nuclei. Since the p densities found in the hydrogen-bonding region do not contribute to the FC term, the P−P coupling constant is small. In contrast, when hydrogen bonding occurs through a lone pair of electrons, both the ground state and interacting excited σ-type triplet states have significant s electron densities in the hydrogen-bonding region.[32]

(2) Because hydrogen bonding occurs through the π system of the acceptor, the orientation of the atoms $P-H\cdots P$ and $P-H\cdots C$ may be far from linear. Nonlinearity also reduces coupling constants, having a most significant effect on two-bond P−P and P−C coupling.

To illustrate that the lack of s electron density in the hydrogen-bonding region of π complexes is the primary factor responsible for the relatively small coupling constants in π complexes, coupling constants have been computed for two complexes that have PH_4^+ as the proton donor ion to acetylene (HC≡CH), with hydrogen bonding occurring at the midpoint of the π bond in one complex and at one of the C atoms in the other. For comparison, coupling constants have also been computed for PH_4^+:C≡O, with hydrogen-bond formation at the C lone pair. The P−C distances in the complexes with C_2H_2 are 3.740 and 3.692 Å, respectively, and 3.735 Å in the PH_4^+:

CO complex. The H−P···C angle is only 9° in the complex in which hydrogen bonding occurs at the midpoint of the acetylene C−C bond, and 0° in the other two complexes, which have linear $P-H^+\cdots C$ arrangements. However, $^{2h}J(P-C)$ for PH_4^+:CO is 58 Hz, while $^{2\pi h}J(P-C)$ for the two PH_4^+:C_2H_2 π complexes is about 5 Hz. The order of magnitude difference between the P−C coupling constants for these two types of complexes is a direct consequence of hydrogen bonding through a C≡C π bond versus a C lone pair of electrons.

Conclusions

An ab initio investigation of complexes formed with protonated P bases as donor ions and the sp-hybridized bases HC≡P and $H_3CC{\equiv}P$ as proton acceptors has been carried out. The following statements are supported by the results of this study.

(1) HC≡P and $H_3CC{\equiv}P$ are very weak bases that are not protonated in the presence of phosphorus bases with sp^2- or sp^3-hybridized P atoms. Hence, only a single minimum exists along the proton-transfer coordinate. These complexes exhibit a variety of structural motifs, but all are stabilized by interactions that occur through the π system of the proton acceptor base.

(2) The protonated homodimers $(HC{\equiv}P)_2H^+$ and $(H_3CC{\equiv}P)_2H^+$ are proton-bound π complexes for which there are two equivalent equilibrium structures. However, the barrier to proton transfer in these two complexes is only 0.5 kcal/mol.

(3) For complexes with HC≡P as the proton acceptor, the protonated homodimer $(HC{\equiv}P)_2H^+$ has the largest binding energy, followed by complexes with sp^2-hybridized $P-H^+$ donors and then complexes with sp^3-hybridized $P-H^+$ donors. This order reflects the decreasing acidity of the conjugate acids of the corresponding protonated bases. With a given donor, the complex with $H_3CC{\equiv}P$ as the proton acceptor is more stable than the complex with HC≡P, a reflection of the greater basicity of $H_3CC{\equiv}P$.

(4) For complexes with sp^2- and sp^3-hybridized $P-H^+$ donors, the P−H bond lengthens and the P−H stretching frequencies are red-shifted relative to the corresponding isolated monomers, although this behavior is not found for complexes with $H_3CPH_3^+$ as the donor, a result of the unusual structures of these complexes. Interaction through the π bond of the proton acceptor bases weakens this bond, as reflected in an increase of the C≡P bond length and a red shift of the C≡P stretching frequency.

(5) The two-bond spin−spin coupling constants $^{2\pi h}J(P-P)$ and $^{2\pi h}J(P-C)$ for $P-H^+\cdots P$ and $P-H^+\cdots C$ interactions are significantly smaller than corresponding coupling constants $^{2h}J(P-P)$ and $^{2h}J(P-C)$ across $P-H^+\cdots P$ and $P-H^+\cdots C$ hydrogen bonds involving lone pairs of electrons at the proton acceptor site. This most probably reflects an absence of significant ground and excited triplet state s electron densities in the hydrogen-bonding region of these π complexes.

Abbreviations

B3LYP, Becke three-parameter hybrid exchange with Lee−Yang−Parr correlation; CASPT2, complete active space, second-order perturbation theory; CASSCF, complete active space, self-consistent field; CBS-QB3, complete basis set, quadratic Becke3; cc-pVDZ and cc-pVTZ, correlation-consistent polarized valence double- and triple-ζ basis sets; CCSD(T), coupled-cluster singles and doubles (with noniterative treatment of triples); MR-ACPF, multireference averaged coupled-pair functional.

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Supporting Information Available: Coordinates of the optimized complexes at the MP2/aug'-cc-pVTZ computational level and full citations for refs 25 and 26. This material is available free of charge via the Internet at http://pubs.acs.org.

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