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Ibon Alkorta* and José Elguero

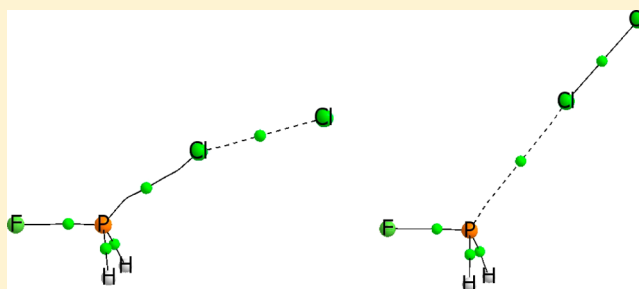
Instituto de Química Médica (IQM-CSIC), Juan de la Cierva, 3, E-28006 Madrid, Spain

Janet E. Del Bene*

Department of Chemistry, Youngstown State University, Youngstown, Ohio 44555, United States

S Supporting Information

ABSTRACT: Ab initio MP2/aug'-cc-pVTZ calculations have been carried out on the halogen-bonded complexes H₂XP:ClF and H₂XP:Cl₂, with X = F, Cl, OH, NC, CN, CCH, CH₃, and H. H₂XP:ClF complexes are stabilized by chlorine-shared halogen bonds with short P–Cl and significantly elongated Cl–F distances. H₂XP:Cl₂ complexes with X = OH and CH₃ form only chlorine-shared halogen bonds, while those with X = H, NC, and CN form only traditional halogen bonds. On the H₂FP:Cl₂, H₂(CCH)P:Cl₂, and H₂ClP:Cl₂ potential surfaces small barriers separate two equilibrium structures, one with a traditional halogen bond and the other with a chlorine-shared bond. The binding energies of H₂XP:ClF and H₂XP:Cl₂ complexes are influenced by the electron-donating ability of H₂XP and the electron accepting ability of ClF and ClCl, the nature of the halogen bond, other secondary interactions, and charge-transfer interactions. Changes in electron populations on P, F, and Cl upon complex formation do not correlate with changes in the chemical shieldings of these atoms. EOM-CCSD spin–spin coupling constants for complexes with chlorine-shared halogen bonds do not exhibit the usual dependencies on distance. ^{2X}J(P–F) and ^{2X}J(P–Cl) for complexes with chlorine-shared halogen bonds do not correlate with P–F and P–Cl distances, respectively. ^{1X}J(P–Cl) values for H₂XP:ClF correlate best with the Cl–F distance, and approach the values of ¹J(P–Cl) for the corresponding cations H₂XPCl⁺. Values of ^{1X}J(P–Cl) for complexes H₂XP:ClCl with chlorine-shared halogen bonds correlate with the binding energies of these complexes. ¹J(F–Cl) and ¹J(Cl–Cl) for complexes with chlorine-shared halogen bonds correlate linearly with the distance between P and the proximal Cl atom. In contrast, ^{2X}J(P–Cl) and ^{1X}J(P–Cl) for complexes with traditional halogen bonds exhibit more normal distance dependencies.



■ INTRODUCTION

Complexes between phosphorus(III) derivatives and halogen molecules have been known for some time. Experimental evidence suggests that halogen-bonded complexes with iodine and bromine may exist in solution, while X-ray crystallographic data provide clear evidence of their existence in the solid state.^{1–5} More recent investigations have reported that chlorine may act in a way similar to the heavier halogens and also form halogen bonds with phosphorus.^{6,7}

The first reported theoretical investigation of a P...Cl halogen bond is a DFT study of (Ph)₃P:Cl₂ which identified three minima on the potential surface.⁸ One minimum corresponds to a phosphane or phosphorus(V) structure, while the other two are complexes stabilized by traditional and chlorine-shared halogen bonds. Other computational studies have found both chlorine-shared and traditional halogen bonds in complexes YCl:CNX and YCl:SiNX, with Y = F or Cl, and X, a variety of substituents.^{9–12} An investigation of XC≡P:ClF complexes¹³ provided two types of halogen-bonded complexes on the potential surfaces. The first consists of complexes in

which the phosphorus acts as a lone-pair donor to Cl, forming either traditional or chlorine-shared halogen bonds depending on the nature of X; the second type consists of complexes in which the XC≡P π bond is the electron donor.

We have also investigated the complexes H₂FP:ClY, with Y = F, NC, Cl, CN, CCH, CH₃, and H,¹⁴ in a search of P...Cl pnictogen-bonded and halogen-bonded complexes, and observed that it is the nature of Y which determines the type of bond formed. Thus, the more electronegative substituents F and NC form only halogen-bonded complexes, while the more electropositive CH₃ and H form only pnictogen-bonded complexes. The remaining substituents Cl, CN, and CCH form two complexes with P...Cl interactions, one pnictogen-bonded and the other halogen-bonded.

In the present study we have extended our search for traditional and chlorine-shared halogen bonds involving different phosphine derivatives to complexes H₂XP:ClF and

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$\text{H}_2\text{XP}:\text{Cl}_2$, with $\text{X} = \text{F}, \text{Cl}, \text{OH}, \text{NC}, \text{CN}, \text{CCH}, \text{CH}_3$, and H . In this paper we report and discuss the structures and binding energies of these complexes, their electronic and bonding properties, and the NMR properties of ^{31}P chemical shieldings and spin–spin coupling constants across halogen bonds.

METHODS

The structures of the isolated monomers and complexes were optimized at second-order Møller–Plesset perturbation theory (MP2)^{15–18} with the aug'-cc-pVTZ basis set.¹⁹ This basis set is derived from the Dunning aug-cc-pVTZ basis set^{20,21} by removing diffuse functions from H atoms. Frequencies were computed to establish that the optimized structures correspond to equilibrium structures on their potential surfaces. In addition, we optimized the transition structures that separate two equilibrium halogen-bonded complexes on three intermolecular surfaces, and the cations H_2XPCl^+ . Optimization and frequency calculations were performed using the Gaussian 09 program.²²

The electron densities of the complexes have been analyzed using the Atoms in Molecules (AIM) methodology^{23–26} employing the AIMAll²⁷ program. The topological analysis of the electron density produces the molecular graph of each complex. This graph identifies the location of electron density features of interest, including the electron density (ρ) maxima associated with the various nuclei, saddle points which corresponds to bond critical points (BCPs), and ring critical points which indicate a minimum electron density within a ring. The zero gradient line which connects a BCP with two nuclei is the bond path. The electron density at the BCP (ρ_{BCP}), the Laplacian of the electron density at the BCP ($\nabla^2\rho_{\text{BCP}}$), and the total energy density (H_{BCP}) are additional useful quantities for characterizing interactions.²⁸

Natural Bond Orbital (NBO)²⁹ MP2/aug'-cc-pVTZ electron populations have been evaluated for monomers and complexes. In addition, the NBO method has been used to analyze the stabilizing charge-transfer interactions using the NBO-6 program.³⁰ Since MP2 orbitals are nonexistent, the charge-transfer interactions have been computed using the B3LYP functional^{31,32} with the aug'-cc-pVTZ basis set at the MP2/aug'-cc-pVTZ geometries, so that at least some electron correlations effects could be included. NBO orbitals have been represented with the Jmol program³³ using the tools developed by Marcel Patek.³⁴

Absolute chemical shieldings have been calculated for monomers and complexes at MP2/aug'-cc-pVTZ using the GIAO approximation.³⁵ Spin–spin coupling constants were evaluated using the equation-of-motion coupled cluster singles and doubles (EOM-CCSD) method in the CI(configuration interaction)-like approximation,^{36,37} with all electrons correlated. For these calculations, the Ahlrichs³⁸ qzp basis set was placed on ^{13}C , ^{15}N , ^{17}O , and ^{19}F , and the qz2p basis set on ^{31}P and ^{35}Cl . The Dunning cc-pVDZ basis set was placed on all ^1H atoms. The EOM-CCSD calculations were performed using ACES II³⁹ on the IBM Cluster 1350 (Glenn) at the Ohio Supercomputer Center.

RESULTS AND DISCUSSION

Structures and Binding Energies. $\text{H}_2\text{XP}:\text{ClF}$ Complexes.

Table S1 of the Supporting Information provides the MP2/aug'-cc-pVTZ structures, total energies, and molecular graphs for complexes $\text{H}_2\text{XP}:\text{ClF}$. Table 1 reports their binding energies

Table 1. Binding Energies (ΔE , $\text{kJ}\cdot\text{mol}^{-1}$) and P–Cl, Cl–F, and P–F Distances (R , Å) in Complexes $\text{H}_2\text{XP}:\text{ClF}$, and P–Cl Distances (R , Å) in Cations H_2XPCl^+

$\text{H}_2\text{XP}:\text{ClF}$, $\text{X} =$	ΔE	$R(\text{P}–\text{Cl})$	$R(\text{P}–\text{F})$	$R(\text{Cl}–\text{F})^a$	$R(\text{P}–\text{Cl})^b$
OH	−92.7	2.054	3.978	1.926	1.939
CH_3	−85.8	2.108	4.017	1.910	1.966
F	−71.1	2.044	3.942	1.903	1.930
CCH	−59.8	2.152	4.018	1.866	1.962
Cl	−58.6	2.107	3.971	1.870	1.950
H	−51.2	2.182	4.033	1.851	1.955
NC	−40.3	2.153	3.986	1.835	1.943
CN	−30.3	2.218	4.029	1.811	1.949

^aThe Cl–F distance in the isolated monomer ClF is 1.638 Å. ^bThe P–Cl distance in the cations H_2XPCl^+ .

along with the P–F, P–Cl, and Cl–F distances. All $\text{H}_2\text{XP}:\text{ClF}$ complexes have chlorine-shared halogen bonds, with short P–Cl and long Cl–F distances. The P–Cl distances vary from 2.044 to 2.218 Å, and are thus approaching the P–Cl distances in the corresponding cations H_2XPCl^+ . These distances are also reported in Table 1, and can be seen to vary from 1.930 to 1.966 Å. The Cl–F distances range from 1.811 to 1.926 Å, significantly longer than the monomer Cl–F distance of 1.638 Å. In general, halogen bonds tend to be linear,⁴⁰ and the bonds in these complexes approach linearity, with F–Cl–P angles varying from 174° to 180°.

The binding energies of $\text{H}_2\text{XP}:\text{ClF}$ complexes are large, and range from $-30 \text{ kJ}\cdot\text{mol}^{-1}$ for $\text{H}_2(\text{CN})\text{P}:\text{ClF}$ to $-93 \text{ kJ}\cdot\text{mol}^{-1}$ for $\text{H}_2(\text{OH})\text{P}:\text{ClF}$. These two complexes are illustrated in Figure 1. The binding energies do not correlate with the P–Cl

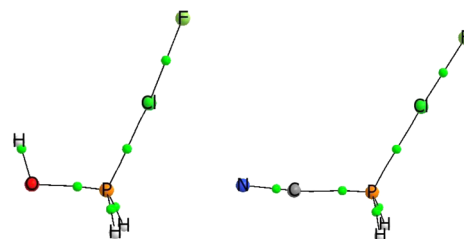


Figure 1. Structures and molecular graphs of $\text{H}_2(\text{OH})\text{P}:\text{ClF}$ with the strongest halogen bond and $\text{H}_2(\text{CN})\text{P}:\text{ClF}$ with the weakest. Bond critical points are indicated by green dots.

or P–F distances, but they do correlate with the Cl–F distance, as illustrated in Figure 2. The order of decreasing binding energy with respect to X is



Factors which influence this unusual order with respect to the substituent will be discussed in some of the sections below. However, at this point it is possible to comment on one of these factors in the two most strongly bound complexes with X equal to OH and CH_3 , two substituents which have very different electronic effects. These binding energies appear to reflect a secondary interaction between the positively charged H atoms of OH and CH_3 and the electron cloud of ClF. To examine this possibility, we have rotated the O–H bond from its *cis* position shown in Figure 1, to the position in which it is *trans* to the P–Cl bond with respect to the P–O bond. Optimization of the *trans* structure leads to a second minimum on the potential surface with a binding energy of $-78 \text{ kJ}\cdot\text{mol}^{-1}$,

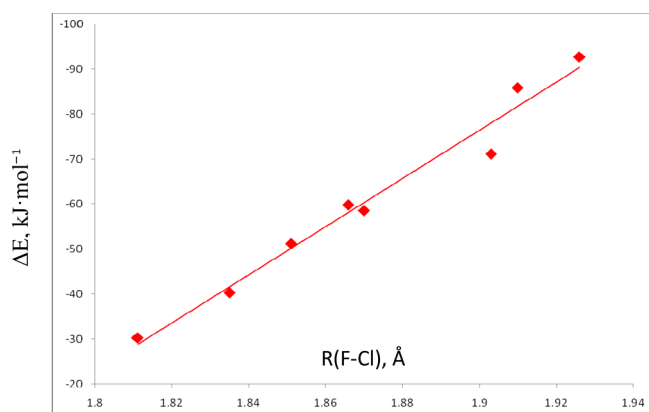


Figure 2. Linear correlation between the binding energy and the Cl–F distance for complexes $H_2XP:ClF$. The correlation coefficient R^2 is 0.974.

14 $\text{kJ}\cdot\text{mol}^{-1}$ less than the *cis*. This result suggests that a secondary electrostatic interaction contributes to the high stabilization energies of $H_2(OH)P:ClF$ and $H_2(CH_3)P:ClF$. The NBO charges on the H atoms of OH and CH_3 in the corresponding H_2XP monomers are 0.522e and 0.250e, respectively, suggesting that these H atoms can interact favorably with a lone pair of electrons on the chlorine of ClF.

The formation of the chlorine-shared $H_2XP:ClF$ complexes may be viewed as a three-step process: (1) dissociation of the ClF molecule: $ClF \rightarrow Cl^+ + F^-$; (2) formation of the $H_2XP:Cl^+$ cation: $H_2XP + Cl^+ \rightarrow H_2XP:Cl^+$; (3) interaction of the cation with F^- : $H_2XP:Cl^+ + F^- \rightarrow H_2XP:Cl^+ \cdots F^-$. The first step is endothermic and common to all complexes, so it does not influence their relative stabilities, while steps 2 and 3 are exothermic and different for each complex. The energies of these two steps as well as the sum of steps 2 and 3 are reported in Table 2. After exclusion of the unique energies for $H_3P:ClF$, which has a relatively small value for step 2 and a relatively large value for step 3, reaction 2 is the dominant contributor to the binding energies of these complexes. Larger values for reaction 2 and smaller values for 3 are found for the more strongly bound complexes, while smaller values for reaction 2 and larger values for 3 are found for the more weakly bound complexes. Nevertheless, neither step 2 nor step 3 energies correlate with the binding energies of these complexes. However, when the energies of steps 2 and 3 are added, the sums correlate perfectly with the binding energies, with a correlation coefficient R^2 of 0.9999. Thus, it is the two interaction energies together which determine the relative binding energies of the chlorine-shared complexes $H_2XP:ClF$.

Table 2. Energies [$E(i)$, $\text{kJ}\cdot\text{mol}^{-1}$] and Relative Energies [$\Delta E(i)$, $\text{kJ}\cdot\text{mol}^{-1}$]^a for Reactions 2 and 3 and Their Sum for Complexes $H_2XP:ClF$

$H_2XP:ClF$ X =	$E(2)$	$\Delta E(2)$	$E(3)$	$\Delta E(3)$	$E(2 + 3)$	$\Delta E(2 + 3)$
OH	−977.8	−130.3	−480.8	67.9	−1458.6	−62.4
CH_3	−996.4	−149.0	−455.3	93.5	−1451.7	−55.5
F	−931.8	−84.3	−505.2	43.5	−1437.0	−40.8
CCH	−947.4	−100.0	−478.2	70.5	−1425.7	−29.5
Cl	−922.8	−75.3	−501.7	47.0	−1424.4	−28.3
H	−23.6	823.9	−1393.5	−844.7	−1417.1	−20.9
NC	−877.0	−29.5	−529.2	19.5	−1406.2	−10.0
CN	−847.5	0.0	−548.7	0.0	−1396.2	0.0

^a ΔE values are relative to $H_2(CN)P:ClF$.

$H_2XP:Cl_2$ Complexes. The intermolecular $H_2(OH)P:Cl_2$ and $H_2(CH_3)P:Cl_2$ surfaces share characteristics with the corresponding $H_2(OH)P:ClF$ and $H_2(CH_3)P:ClF$ surfaces, as both $H_2(OH)P:Cl_2$ and $H_2(CH_3)P:Cl_2$ are stabilized by chlorine-shared halogen bonds. However, the surfaces of the remaining complexes are significantly different. There are three surfaces, $H_2FP:Cl_2$, $H_2(CCH)P:Cl_2$, and $H_2ClP:Cl_2$, which exhibit two minima along the halogen-bonding coordinate. One minimum is found at short P–Cl and long Cl–Cl distances, and corresponds to a complex stabilized by a chlorine-shared halogen bond. The second minimum is found at long P–Cl and short Cl–Cl distances, and corresponds to a complex with a traditional halogen bond. The structures and molecular graphs of the two $H_2FP:Cl_2$ complexes are illustrated in Figure 3. The remaining three surfaces $H_3P:Cl_2$, $H_2(NC)P:Cl_2$, and $H_2(CN)P:Cl_2$ have only a single minimum along the halogen-bonding coordinate with a traditional halogen bond.

Table 3 presents the binding energies of complexes $H_2XP:Cl_2$ with chlorine-shared and traditional halogen bonds. $H_2(OH)P:Cl_2$ and $H_2(CH_3)P:Cl_2$ which form only chlorine-shared halogen bonds have the largest binding energies of $−34 \text{ kJ}\cdot\text{mol}^{-1}$, more than twice the binding energy of any other

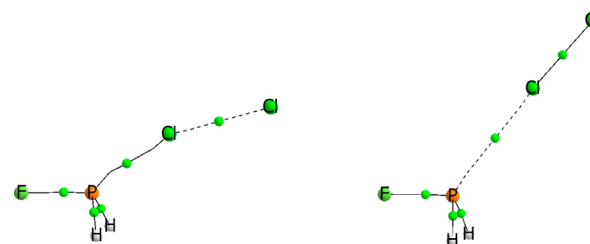


Figure 3. Molecular graphs of the chlorine-shared (left) and traditional (right) halogen-bonded $H_2FP:Cl_2$ complexes.

Table 3. Binding Energies (ΔE , $\text{kJ}\cdot\text{mol}^{-1}$) of Complexes $H_2XP:Cl_2$ with Chlorine-Shared (S) and Traditional (T) Halogen Bonds

$H_2XP:Cl_2$, X =	$\Delta E(S)$	$\Delta E(T)$
OH	−34.1	
CH_3	−33.5	
F	−15.1	−12.8
CCH	−13.0	−15.7
Cl	−10.3	−13.4
H		−14.3
NC		−11.0
CN		−10.4

complex in this series. These large binding energies may reflect the stabilizing secondary interactions between the OH and CH₃ hydrogens and the proximal Cl of ClCl, also found in the corresponding complexes with ClF. The binding energies of H₂XP:Cl₂ complexes with chlorine-shared halogen bonds are significantly less than the binding energies of the corresponding complexes H₂XP:ClF, although the order of decreasing binding energy is the same for both series. The chlorine-shared halogen-bonded complex H₂FP:Cl₂ has a binding energy of $-15 \text{ kJ}\cdot\text{mol}^{-1}$, which is $2 \text{ kJ}\cdot\text{mol}^{-1}$ greater than that of the corresponding complex with a traditional halogen bond. However, the traditional halogen-bonded complexes H₂(CCH)P:Cl₂ and H₂CIP:Cl₂ have binding energies of -16 and $-13 \text{ kJ}\cdot\text{mol}^{-1}$, respectively, which makes them $3 \text{ kJ}\cdot\text{mol}^{-1}$ more stable than the corresponding complexes with chlorine-shared halogen bonds. Only traditional halogen-bonded complexes are found on the H₃P:Cl₂, H₂(NC)P:Cl₂, and H₂(CN)P:Cl₂ surfaces, with binding energies of -14 , -11 , and $-10 \text{ kJ}\cdot\text{mol}^{-1}$, respectively. It is interesting to note that the order of decreasing binding energies for complexes with traditional halogen bonds is different from the order for chlorine-shared halogen bonds. For the traditional halogen-bonded complexes, binding energies decrease with respect to X in the order

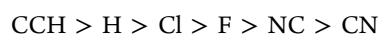


Table 4 reports Cl–Cl and proximal and distal P–Cl distances, as well as P–Cl–Cl and A–P–Cl angles, with A the

Table 4. P–Cl and Cl–Cl Distances (*R*, Å) and P–Cl–Cl and A–P–Cl Angles (\angle , °) in H₂XP:Cl₂ Complexes with Traditional and Chlorine-Shared Halogen Bonds

H ₂ XP:Cl ₂	<i>R</i> (P–Cl) ^a		<i>R</i> (P–Cl) ^b		<i>R</i> (Cl–Cl) ^c	
	shared	traditional	shared	traditional	shared	traditional
X = OH	2.133		4.477		2.353	
CH ₃	2.221		4.526		2.308	
F	2.157	3.061	4.351	5.079	2.278	2.022
CCH	2.356	2.969	4.571	4.999	2.216	2.031
Cl	2.234	3.048	4.435	5.068	2.247	2.022
H		3.048		5.072		2.025
NC		3.136		5.148		2.014
CN		3.170		5.179		2.011
H ₂ XP:Cl ₂	\angle P–Cl–Cl		\angle A–P–Cl ^d			
	shared	traditional	shared	traditional		
X = OH	173		109			
CH ₃	176		110			
F	158	175	143	127		
CCH	178	177	120	111		
Cl	163	177	140	108		
H		180		122		
NC		177		108		
CN		177		108		

^aProximal Cl that is bonded directly to P. ^bDistal Cl. ^cCl–Cl bond length in the isolated monomer is 1.999 Å. ^dA is the atom of X directly bonded to P.

atom of X directly bonded to P. The data of Table 4 show the significant differences among these distances in traditional and chlorine-shared halogen bonds. The distance between P and the proximal Cl is 2.4 Å or less if the halogen bond is chlorine-shared, and 3.0 Å or greater if the halogen bond is traditional. The distance between P and the distal Cl is 4.6 Å or less in

complexes with chlorine-shared halogen bonds, and 5.0 to 5.2 Å for traditional halogen bonds. The Cl–Cl bond distance increases to 2.2 Å or greater in complexes with chlorine-shared halogen bonds, but is similar to the monomer distance of 2.0 Å when the halogen bond is traditional. Neither of the two P–Cl distances in complexes with chlorine-shared halogen bonds correlates with the binding energies of these complexes. The binding energies do show a tendency to increase linearly as the Cl–Cl distance increases, but the correlation coefficient R^2 is only 0.779. In contrast, increasing binding energies of complexes with traditional halogen bonds correlate linearly with decreasing proximal and distal P–Cl distances, and with increasing Cl–Cl distance, with correlation coefficients R^2 of 0.959, 0.949, and 0.983, respectively.

Table 4 also reports the P–Cl–Cl and A–P–Cl angles. In complexes with chlorine-shared halogen bonds except H₂FP:Cl₂ and H₂CIP:Cl₂, the P–Cl–Cl angle approaches linearity, and the A–P–Cl angles are between 109° and 120°. However, in the H₂FP:Cl₂ and H₂CIP:Cl₂ complexes these angles are significantly different with P–Cl–Cl angles of 158° and 163°, and A–P–Cl angles of 143° and 140°, respectively. The increased values of the A–P–Cl angle move both Cl atoms away from the substituents F and Cl, while the decreased values of the P–Cl–Cl angle move the distal Cl further from these substituents. These differences reduce the interaction between the substituents F and Cl and the diffuse electron cloud of Cl₂. Such differences, as well as the lack of correlation between binding energies and P–Cl distances in complexes with chlorine-shared halogen bonds, suggest that the stabilities of complexes with these bonds reflect interactions in addition to the halogen bond itself.

The traditional halogen bonds found in complexes H₂XP:ClCl are also linear, with P–Cl–Cl angles between 175° and 180°. While the H–P–H and A–P–H angles of H₂XP in the complexes vary between 94° and 98°, the A–P–Cl angles are between 108° and 111° for four of the complexes. That is, for these the covalent P–A bond and the P...Cl halogen bond have a tetrahedral arrangement. The two exceptions are H₂FP:ClCl and H₃P:ClCl which have A–P–Cl angles of 127° and 122°, respectively. The value of 127° suggests a repulsive interaction between F and ClCl, similar to but less repulsive than that found for the corresponding H₂FP:ClCl complex with a chlorine-shared halogen bond and a shorter distance between the substituent F and the Cl atoms. The structural differences between the two H₂FP:Cl₂ complexes can be seen in Figure 3.

Why does the H–P–Cl angle in H₃P:ClCl also have a large value? In order to answer this question, we have examined the H–P–H and A–P–H angles in all of the monomers, and have determined the angle between the P–A bond and the phosphorus lone pair. We have approximated the latter as the angle between the P–A bond and a line connecting the P atom to the minimum value of the MEP for each monomer. These values are between 114° and 118° for all monomers except PH₃, in which case it is 122.3°. Thus, the value of this angle is essentially unchanged in the H₃P:ClCl complex, and reflects its C_{3v} symmetry. The A–P–Cl angles in four of the complexes are reduced relative to the corresponding monomers, but increased in H₂FP:ClCl to reduce repulsion, as noted above.

Two distinct halogen-bonded complexes have been identified on the H₂FP:Cl₂, H₂(CCH)P:Cl₂, and H₂CIP:Cl₂ potential surfaces, one with a traditional halogen bond, and the other with a chlorine-shared bond. The P–Cl and Cl–Cl distances of

the transition structures which separate them and the binding energies of these structures are given in Table 5. For $\text{H}_2\text{FP}:\text{Cl}_2$,

Table 5. Binding Energies (ΔE , $\text{kJ}\cdot\text{mol}^{-1}$) and P–Cl and Cl–Cl Distances (R , Å) of Transition Structures between Traditional and Chlorine-Shared Equilibrium Structures on $\text{H}_2\text{FP}:\text{Cl}_2$, $\text{H}_2(\text{CCH})\text{P}:\text{Cl}_2$, and $\text{H}_2\text{ClP}:\text{Cl}_2$ Potential Surfaces

complex	ΔE	$R(\text{P}–\text{Cl})^a$	$R(\text{Cl}–\text{Cl})$
$\text{H}_2\text{FP}:\text{Cl}_2$	−9.9	2.478	2.115
$\text{H}_2(\text{CCH})\text{P}:\text{Cl}_2$	−12.9	2.469	2.160
$\text{H}_2\text{ClP}:\text{Cl}_2$	−10.3	2.444	2.143

^aDistance between P and the proximal Cl.

the barrier to the conversion of the less stable complex with the traditional halogen bond to the more stable structure with the chlorine-shared bond is $2.9\text{ kJ}\cdot\text{mol}^{-1}$, while the reverse barrier is $5.2\text{ kJ}\cdot\text{mol}^{-1}$. Thus, the Cl_2 molecule should oscillate easily between the two minima. In contrast, the barriers for the conversion of the less stable chlorine-shared structures of $\text{H}_2(\text{CCH})\text{P}:\text{Cl}_2$ and $\text{H}_2\text{ClP}:\text{Cl}_2$ to the more stable structures with traditional halogen bonds are no more than $0.1\text{ kJ}\cdot\text{mol}^{-1}$. This indicates that the chlorine-shared structures exist in extremely shallow minima, so that only the traditional halogen-bonded complexes would exist even at very low temperatures. Nevertheless, all three transition structures have similar P–Cl distances around 2.46 Å and Cl–Cl distances near 2.14 Å .

Electronic Properties. The topological analysis of the electron density of each complex shows an intermolecular bond critical point (BCP) connecting the phosphorus atom and the proximal Cl atom, as seen in Table S1 of the Supporting Information. The electron densities at the BCPs (ρ_{BCP}) in the chlorine-shared complexes are large, with values between 0.081 and 0.147 au. An excellent exponential relationship with a correlation coefficient of 0.999 is found between ρ_{BCP} and the P–Cl distance, in agreement with previous reports that show similar relationships for other intermolecular interactions.^{41–49} All $\text{H}_2\text{XP}:\text{ClF}$ complexes and the two chlorine-shared complexes $\text{H}_2(\text{OH})\text{P}:\text{Cl}_2$ and $\text{H}_2\text{FP}:\text{Cl}_2$ with the shortest intermolecular distances have negative values of the total energy density H_{BCP} and the Laplacian. The negative values of these two parameters are indicative of the partial covalent character of the $\text{P}\cdots\text{Cl}$ interaction. The $\text{H}_2(\text{CH}_3)\text{P}:\text{Cl}_2$, $\text{H}_2(\text{CCH})\text{P}:\text{Cl}_2$, and $\text{H}_2(\text{Cl})\text{P}:\text{Cl}_2$ complexes with chlorine-shared halogen bonds have negative values of the energy density but positive values of the Laplacian, indicating that the covalent character of the $\text{P}\cdots\text{Cl}$ interaction is reduced relative to

$\text{H}_2\text{XP}:\text{ClF}$, $\text{H}_2(\text{OH})\text{P}:\text{Cl}_2$, and $\text{H}_2\text{FP}:\text{Cl}_2$. The $\text{H}_2\text{XP}:\text{Cl}_2$ complexes with traditional halogen bonds have positive values of both the Laplacian and the energy density, and therefore little if any $\text{P}\cdots\text{Cl}$ covalent character.

The formation of chlorine-shared halogen bonds leads to a significant reorganization of electron density. The changes in the atomic charges in the complexes relative to the isolated monomers are reported in Table 6. In the chlorine-shared complexes with ClF, the P atom, which is positively charged in the monomers and the electron-pair donor in the complexes, has an increased positive charge in the complexes ranging from 0.339e in $\text{H}_2(\text{CN})\text{P}:\text{ClF}$ to 0.558e in $\text{H}_2(\text{OH})\text{P}:\text{ClF}$. The Cl atom of ClF remains positively charged, although this charge is reduced relative to the monomer charge of 0.351e. The vast majority of the charge transferred from P is acquired by F, with its negative charge increasing by 0.518e in $\text{H}_2(\text{CN})\text{P}:\text{ClF}$ to 0.676e in $\text{H}_2(\text{OH})\text{P}:\text{ClF}$. A similar pattern is observed in the chlorine-shared complexes with Cl_2 , with P losing a significant amount of electron density and the distal Cl acquiring most of this density. However, unlike the ClF complexes, the proximal Cl also acquires some density, and becomes negatively charged in the complexes. In all chlorine-shared complexes, the total electron density gained by ClF and Cl_2 is noticeably greater than the electron density lost by P, which indicates that charge is also lost by other atoms in the H_2XP molecule. In complexes with traditional halogen bonds with Cl_2 , P loses electron density and both Cl atoms gain electron density, but the changes in atomic charges are much smaller than those observed in the complexes with chlorine-shared halogen bonds.

The Wiberg bond orders⁵⁰ for the $\text{P}\cdots\text{Cl}$, Cl–F, and Cl–Cl bonds in $\text{H}_2\text{XP}:\text{ClF}$ and $\text{H}_2\text{XP}:\text{Cl}_2$ complexes are reported in Table 7. Complexes with chlorine-shared halogen bonds have large bond orders for the $\text{P}\cdots\text{Cl}$ bonds, ranging from 0.70 to 1.00 in $\text{H}_2\text{XP}:\text{ClF}$ complexes and from 0.48 to 0.76 in $\text{H}_2\text{XP}:\text{Cl}_2$ complexes. These strong interactions weaken the Cl–F and Cl–Cl bonds, with the Cl–F bond orders varying between 0.33 and 0.50, and the Cl–Cl bond orders between 0.41 and 0.61. By contrast, $\text{P}\cdots\text{Cl}$ bond orders are about 0.1 and Cl–Cl bond orders are greater than 0.92 in complexes with traditional halogen bonds.

The structures, binding energies, and the Wiberg bond orders of complexes with chlorine-shared halogen bonds suggest that the $\text{P}\cdots\text{Cl}$ interaction is approaching a covalent bond. In fact, when computing the stabilizing charge transfer energies, the NBO method treats all but three of these complexes as two ions, $\text{H}_2\text{XP}:\text{Cl}^+$ with either F^- or Cl^- . Only three complexes, $\text{H}_2(\text{NC})\text{P}:\text{ClF}$, $\text{H}_2(\text{CCH})\text{P}:\text{Cl}_2$, and

Table 6. NBO MP2/aug'-cc-pVTZ Changes in Charges (δe , au) on P, Cl, and F upon Formation of Complexes $\text{H}_2\text{XP}:\text{Cl}_2$ and $\text{H}_2\text{XP}:\text{ClF}$

X =	$\text{H}_2\text{XP}:\text{ClF}^a$			$\text{H}_2\text{XP}:\text{Cl}_2$ chlorine-shared			$\text{H}_2\text{XP}:\text{Cl}_2$ traditional		
	$\delta e(\text{P})$	$\delta e(\text{Cl})$	$\delta e(\text{F})$	$\delta e(\text{P})$	$\delta e(\text{Cl})^b$	$\delta e(\text{Cl})$	$\delta e(\text{P})$	$\delta e(\text{Cl})^b$	$\delta e(\text{Cl})$
OH	0.558	0.005	−0.676	0.528	−0.152	−0.507			
CH_3	0.528	0.007	−0.645	0.464	−0.167	−0.426			
F	0.488	0.038	−0.654	0.333	−0.131	−0.331	0.028	−0.019	−0.041
CCH	0.439	0.032	−0.584	0.318	−0.155	−0.271	0.029	−0.019	−0.052
Cl	0.389	0.048	−0.594	0.274	−0.135	−0.282	0.005	−0.013	−0.036
H	0.473	0.031	−0.571				0.023	−0.011	−0.046
NC	0.394	0.063	−0.559				0.007	−0.012	−0.021
CN	0.339	0.079	−0.518				−0.001	−0.008	−0.017

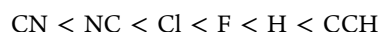
^aCharges on Cl and F are ± 0.351 au in the monomer. ^bProximal Cl atom that forms the $\text{P}\cdots\text{Cl}$ halogen bond.

Table 7. Wiberg Bond Orders for P...Cl, Cl–F, and Cl–Cl Bonds in Halogen-Bonded Complexes

Complexes with X =	H ₂ XP:ClF		H ₂ XP:Cl ₂ chlorine-shared		H ₂ XP:Cl ₂ traditional	
	P–Cl	Cl–F ^a	P–Cl	Cl–Cl ^b	P–Cl	Cl–Cl ^b
OH	0.95	0.33	0.76	0.41		
CH ₃	0.86	0.36	0.64	0.47		
F	1.00	0.34	0.74	0.49	0.11	0.95
CCH	0.79	0.42	0.48	0.61	0.12	0.93
Cl	0.87	0.40	0.62	0.55	0.09	0.96
H	0.77	0.44			0.11	0.95
NC	0.81	0.44			0.07	0.98
CN	0.70	0.50			0.06	0.99

^aBond order in ClF is 0.90. ^bBond order in Cl₂ is 1.05.

H₂ClP:Cl₂, are described as a pair of interacting neutral molecules, but this description leads to P(lp) → σ*Cl–F and P(lp) → σ*Cl–Cl charge-transfer energies that are unreasonably high. The NBO analysis does indicate that for H₂XP:Cl₂ complexes with traditional halogen bonds, there is only one significant charge transfer interaction which occurs from the lone pair on P to the σ* Cl–Cl orbital. These stabilizing charge-transfer energies are reported in Table 8, and vary from 15 kJ·mol^{−1} for H₂(CN)P:Cl₂ to 32 kJ·mol^{−1} for H₂(CCH)P:Cl₂. The charge-transfer energies increase in the order



which, except for a reversal of Cl and F, is the same as the order of increasing binding energies of the corresponding complexes. These data indicate that charge transfer is an important factor in the stabilization of halogen-bonded complexes.

Table 8. Charge-Transfer Energies (kJ·mol^{−1}) in H₂XP:Cl₂ Complexes with Traditional Halogen Bonds

H ₂ XP:Cl ₂	P(lp) → σ*Cl–Cl
X = F	23.5
CCH	32.2
Cl	21.8
H	25.7
NC	17.1
CN	14.5

Chemical Shieldings. The chemical shieldings of ³¹P, ¹⁹F, and ³⁵Cl in the monomers and complexes are reported in Table 9. As noted above, the formation of a chlorine-shared halogen bond leads to a loss of electron density by P and an increase in the positive charge on this atom. This generally leads to a decrease in the ³¹P chemical shielding in the complex relative to the corresponding H₂XP molecule, except for complexes with chlorine-shared halogen bonds with X = OH and F, the H₂ClP:Cl₂ complex with a chlorine-shared halogen bond, and H₂FP:Cl₂ with a traditional halogen bond.

Although the Cl atom of ClF loses electron density and experiences a relatively small increase in its positive charge upon complex formation, its chemical shielding increases dramatically from −410 ppm in the monomer to between 676 ppm in H₂(CN)P:ClF and 855 ppm in H₂(CH₃)P:ClF. The proximal Cl in the complexes H₂XP:Cl₂ with chlorine-shared halogen bonds experiences a significant decrease in positive charge upon complex formation, and its chemical shielding also increases, but to a much lesser extent compared to the complexes with ClF. Thus, in the Cl₂ molecule the chemical shielding is 702 ppm, and upon complex formation it ranges from 811 to 956 ppm. The F atom of ClF gains significant electron density upon complexation, but its chemical shielding decreases from 677 ppm in ClF to less than 100 ppm in the complexes. The distal Cl in H₂XP:Cl₂ complexes with chlorine-shared halogen bonds gains significant electron density upon complexation, but its chemical shielding also decreases from 702 ppm in the monomer to between 282 and 519 in the complexes. As might be anticipated, the weaker interactions in the H₂XP:Cl₂ complexes with traditional halogen bonds have much smaller changes in electron densities and chemical shieldings relative to the corresponding monomers. The positive charges on P tend to increase slightly upon complexation, and the ³¹P chemical shieldings decrease by 1 to 15 ppm, except for H₂FP:Cl₂, in which case it increases by 4 ppm. While both Cl atoms experience a small increase in electron density, the chemical shielding of the proximal Cl increases from 12 to 26 ppm, while that of the distal Cl decreases. These data indicate that electron density changes upon complexation do not correlate with changes in chemical shieldings.

Spin–Spin Coupling Constants. Table S2 of the Supporting Information provides values of the components of coupling constants ^{2X}J(P–F), ^{2X}J(P–Cl), ^{1X}J(P–Cl), ¹J(F–Cl), and

Table 9. Absolute Chemical Shieldings (ppm) of ³¹P, ¹⁹F, and ³⁵Cl in Monomers and Complexes

	isolated H ₂ XP	H ₂ XP:ClF			H ₂ XP:Cl ₂ (chlorine-shared halogen bonds)			H ₂ XP:Cl ₂ (traditional halogen bonds)		
	³¹ P	³¹ P	³⁵ Cl	¹⁹ F	³¹ P	³⁵ Cl ^a	³⁵ Cl ^b	³¹ P	³⁵ Cl ^a	³⁵ Cl ^b
ClF/Cl ₂			−410.3	676.5		702.1	702.1		702.1	702.1
H ₂ (OH)P:ClY	340.2	345.7	789.5	73.0	371.7	878.2	518.8			
H ₂ (CH ₃)P:ClY	548.6	441.7	855.2	70.2	473.3	956.1	467.8			
H ₂ FP:ClY	272.8	313.8	744.4	63.9	356.6	811.3	299.7	276.5	715.4	656.8
H ₂ (CCH)P:ClY	566.9	478.9	775.9	59.0	518.0	891.8	391.4	554.1	723.9	637.8
H ₂ ClP:ClY	420.4	387.7	731.4	58.7	427.5	884.5	281.7	419.9	714.2	652.7
H ₃ P:ClY	633.2	515.4	815.2	63.5				618.6	728.0	650.2
H ₂ (NC)P:ClY	454.5	423.0	697.0	71.4				452.4	721.1	654.7
H ₂ (CN)P:ClY	577.7	503.1	675.6	79.8				570.9	722.0	656.2
H ₃ PCl ⁺		394.1	1013.3							
H ₂ PCl		420.4	1108.9							

^aProximal Cl atom. ^bDistal Cl atom.

$^1J(\text{Cl}-\text{Cl})$ for complexes $\text{H}_2\text{XP}:\text{ClF}$ and $\text{H}_2\text{XP}:\text{Cl}_2$. For complexes with chlorine-shared halogen bonds, the FC terms are the largest terms contributing to $^{2X}J(\text{F}-\text{P})$ and $^{2X}J(\text{Cl}-\text{P})$, but they are not good approximations to these coupling constants because of non-negligible PSO and SD terms. PSO, FC, and SD terms make positive contributions to these two-bond coupling constants, except for $\text{H}_2\text{FP}:\text{Cl}_2$ and $\text{H}_2\text{ClP}:\text{Cl}_2$, in which case the SD term is negative and fortuitously cancels the PSO term. The FC terms also make positive contributions to $^{1X}J(\text{P}-\text{Cl})$ except for the complexes with $\text{X} = \text{F}$. The FC terms are reduced by the contributions of the PSO terms which are always negative. Similarly, PSO, FC, and SD terms contribute to $^1J(\text{F}-\text{Cl})$ and $^1J(\text{Cl}-\text{Cl})$. Hence, it is necessary to evaluate all terms except for the DSO terms when computing the values of these coupling constants.

The situation is quite different for complexes $\text{H}_2\text{XP}:\text{Cl}_2$ with traditional halogen bonds. $^{2X}J(\text{Cl}-\text{P})$ values are dominated by the FC terms, but owing to their relatively small values, the FC terms may or may not be good approximations to total J . In contrast, the FC terms are excellent approximations to $^{1X}J(\text{Cl}-\text{P})$. Finally, $^1J(\text{Cl}-\text{Cl})$ values are dominated by the positive PSO terms followed by the SD terms. The FC terms make small negative contributions to total J .

Components of $^1J(\text{P}-\text{Cl})$ for cations H_2XPCl^+ are reported in Table S3 of the Supporting Information. In contrast to $^{1X}J(\text{P}-\text{Cl})$ for $\text{H}_2\text{XP}:\text{ClF}$, the FC terms in the cations are large and negative. The PSO terms also make negative contributions to $^1J(\text{P}-\text{Cl})$, while the SD terms are smaller and positive. Although the FC terms are dominant, they are not good approximations to $^1J(\text{P}-\text{Cl})$.

$\text{H}_2\text{XP}:\text{ClF}$ Complexes. Table 10 provides values of $^{2X}J(\text{F}-\text{P})$ for the complexes $\text{H}_2\text{XP}:\text{ClF}$ with chlorine-shared halogen bonds. The values of this coupling constant are very large,

Table 10. $^{2X}J(\text{F}-\text{P})$, $^{2X}J(\text{Cl}-\text{P})$, $^{1X}J(\text{Cl}-\text{P})$, $^1J(\text{F}-\text{Cl})$, and $^1J(\text{Cl}-\text{Cl})$ (Hz) in Complexes $\text{H}_2\text{XP}:\text{ClF}$ and $\text{H}_2\text{XP}:\text{Cl}_2$

$\text{H}_2\text{XP}:\text{ClF}$	$^{2X}J(\text{F}-\text{P})$	$^{1X}J(\text{Cl}-\text{P})$	$^1J(\text{F}-\text{Cl})^a$
$\text{X} = \text{OH}$	1089.4	-46.4	539.6
CH_3	1094.1	38.4	579.4
F	1293.5	-6.3	544.1
CCH	1191.7	163.3	605.2
Cl	1351.4	194.6	576.4
H	1158.5	213.4	621.7
NC	1299.7	244.2	595.3
CN	1125.3	339.3	625.3
$\text{H}_2\text{XP}:\text{Cl}_2^b$	$^{2X}J(\text{Cl}-\text{P})$	$^{1X}J(\text{Cl}-\text{P})$	$^1J(\text{Cl}-\text{Cl})^c$
$\text{X} = \text{OH}$	148.6	-56.9	72.9
CH_3	153.4	111.2	80.0
F	170.9	421.0	75.4
CCH	129.5	402.1	87.8
Cl	151.3	570.5	82.3
$\text{H}_2\text{XP}:\text{Cl}_2^d$	$^{2X}J(\text{Cl}-\text{P})$	$^{1X}J(\text{Cl}-\text{P})$	$^1J(\text{Cl}-\text{Cl})^c$
$\text{X} = \text{F}$	11.7	245.4	97.4
CCH	17.2	255.5	97.5
Cl	10.9	225.3	97.8
H	12.4	224.3	97.8
NC	6.2	172.5	97.7
CN	4.2	150.2	97.9

^a $^1J(\text{F}-\text{Cl})$ for the monomer is 798.4 Hz. ^bComplexes with chlorine-shared halogen bonds. ^c $^1J(\text{Cl}-\text{Cl})$ for the monomer is 99.6 Hz.

^dComplexes with traditional halogen bonds.

ranging from 1090 Hz for $\text{H}_2(\text{OH})\text{P}:\text{ClF}$ to 1351 Hz for $\text{H}_2\text{ClP}:\text{ClF}$. However, $^{2X}J(\text{F}-\text{P})$ is not a function of the $\text{F}-\text{P}$ distance, nor does it correlate with the $\text{Cl}-\text{P}$ or $\text{Cl}-\text{F}$ distances. This lack of correlation may be a reflection of the nature of this coupling constant, which depends on ground and excited state s and p electron densities, since terms in addition to the FC terms are important contributors to total J . This lack of correlation also reflects the ionic character of these complexes.

Coupling constants $^{1X}J(\text{Cl}-\text{P})$ are also reported in Table 10. These coupling constants vary from -46 Hz in $\text{H}_2(\text{OH})\text{P}:\text{ClF}$ to 339 Hz in $\text{H}_2(\text{CN})\text{P}:\text{ClF}$. $^{1X}J(\text{Cl}-\text{P})$ does exhibit a linear dependence on the $\text{Cl}-\text{P}$ distance, but the correlation coefficient R^2 is only 0.840. However, Figure 4 indicates a

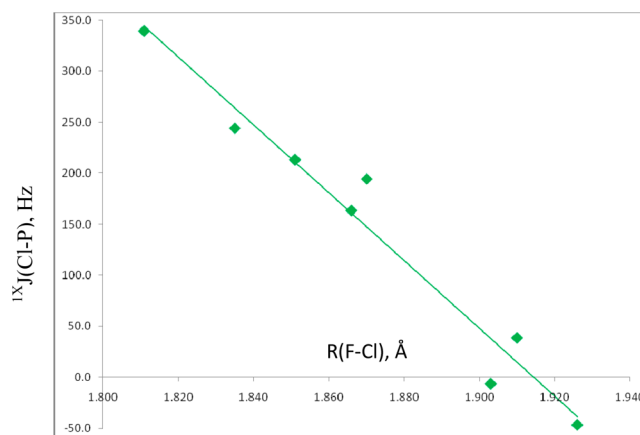


Figure 4. $^{1X}J(\text{Cl}-\text{P})$ vs the $\text{F}-\text{Cl}$ distance. The correlation coefficient $R^2 = 0.958$.

correlation between decreasing $^{1X}J(\text{Cl}-\text{P})$ and increasing $\text{F}-\text{Cl}$ distance. Since increasing $\text{F}-\text{Cl}$ distance is associated with increasing covalency of the $\text{P}-\text{Cl}$ bond, values of $^{1X}J(\text{P}-\text{Cl})$ approach the negative values of $^1J(\text{P}-\text{Cl})$ for the cations

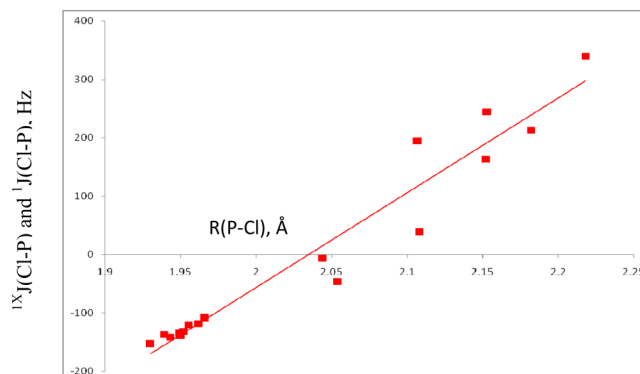


Figure 5. $^{1X}J(\text{Cl}-\text{P})$ for $\text{H}_2\text{XP}:\text{ClF}$ and $^1J(\text{P}-\text{Cl})$ for H_2XPCl^+ vs the $\text{P}-\text{Cl}$ distance. Although the data for the complexes at longer $\text{P}-\text{Cl}$ distances are scattered with $R^2 = 0.840$, the correlation coefficient for the two sets together is 0.942.

H_2XPCl^+ , as illustrated in Figure 5. The very different nature of $^{1X}J(\text{P}-\text{Cl})$ and $^1J(\text{P}-\text{Cl})$ in terms of their PSO and FC contributions may be attributed to the difference between the $\text{P}-\text{Cl}$ distances in the complexes and cations, and the absence of a highly negatively charged F atom in the cations. It should also be noted that since the binding energies of complexes

$\text{H}_2\text{XP}:\text{ClF}$ correlate linearly with the $\text{Cl}-\text{F}$ distance, $^1J(\text{Cl}-\text{P})$ and the binding energies also correlate with an R^2 value of 0.903.

$^1J(\text{F}-\text{Cl})$ is the third coupling constant of interest. It exhibits a poor correlation with the $\text{F}-\text{Cl}$ distance, with a correlation coefficient of only 0.732. However, $^1J(\text{F}-\text{Cl})$ increases linearly as the $\text{P}-\text{Cl}$ distance increases, with a correlation coefficient R^2 of 0.965. Thus, in these complexes with chlorine-shared halogen bonds to P, there exists an unusual dependence of coupling constants on distance, with $^1J(\text{F}-\text{Cl})$ correlating with the $\text{P}-\text{Cl}$ distance, $^1J(\text{Cl}-\text{P})$ correlating with the $\text{F}-\text{Cl}$ distance, and $^{2X}J(\text{F}-\text{P})$ showing little correlation with any distance.

$\text{H}_2\text{XP}:\text{Cl}_2$ with Chlorine-Shared Halogen Bonds. Coupling constants $^{2X}J(\text{P}-\text{Cl})$, $^1J(\text{P}-\text{Cl})$, and $^1J(\text{Cl}-\text{Cl})$ for complexes $\text{H}_2\text{XP}:\text{Cl}_2$ with chlorine-shared halogen bonds are also reported in Table 10. $^{2X}J(\text{P}-\text{Cl})$ varies from 130 Hz for $\text{H}_2(\text{CCH})\text{P}:\text{Cl}_2$ to 171 Hz for $\text{H}_2(\text{F})\text{P}:\text{Cl}_2$. Increasing $^{2X}J(\text{P}-\text{Cl})$ tends to correlate linearly with decreasing $\text{P}-\text{Cl}$ distance, with Cl being the distal Cl involved in the coupling, although the correlation coefficient is only 0.786.

Coupling constants $^1J(\text{P}-\text{Cl})$ exhibit a very large range of values, from -57 Hz for $\text{H}_2(\text{OH})\text{P}:\text{Cl}_2$ to $+570$ Hz for $\text{H}_2(\text{Cl})\text{P}:\text{Cl}_2$. This coupling constant does not correlate with the distance between P and the proximal Cl, but does show some correlation with the $\text{Cl}-\text{Cl}$ distance, although the correlation coefficient R^2 is only 0.750. The very large range of values for $^1J(\text{P}-\text{Cl})$ along with the negative value of -57 Hz for $\text{H}_2(\text{OH})\text{P}:\text{Cl}_2$ are indicators of the changing degree of covalency of the $\text{P}-\text{Cl}$ interaction in these complexes. Although $^1J(\text{P}-\text{Cl})$ values do not correlate with the distance between P and the proximal Cl bonded to it, they do correlate with the binding energies of these complexes, as can be seen in Figure 6.

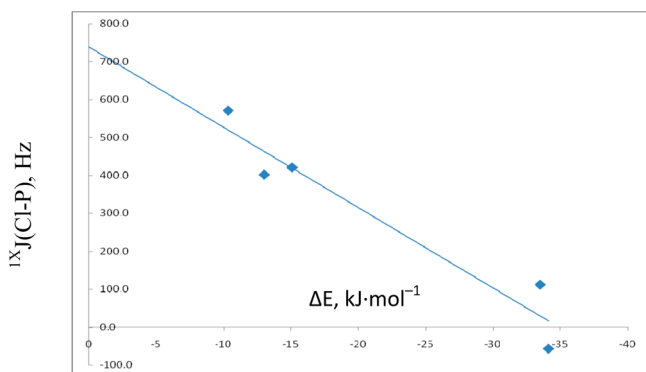


Figure 6. $^1J(\text{Cl}-\text{P})$ versus the binding energies of $\text{H}_2\text{XP}:\text{Cl}_2$ complexes with chlorine-shared halogen bonds. The correlation coefficient $R^2 = 0.930$.

The third coupling constant of interest in these complexes is $^1J(\text{Cl}-\text{Cl})$. Values of this coupling constant are reduced relative to the monomer value of 99.6 Hz, varying from 73 to 88 Hz. Like $^1J(\text{F}-\text{Cl})$ for $\text{H}_2\text{XP}:\text{ClF}$ complexes, $^1J(\text{Cl}-\text{Cl})$ correlates linearly not with the $\text{Cl}-\text{Cl}$ distance, but with the distance between P and the proximal Cl, with a correlation coefficient R^2 of 0.964.

$\text{H}_2\text{XP}:\text{Cl}_2$ with Traditional Halogen Bonds. Coupling constants $^{2X}J(\text{P}-\text{Cl})$, $^1J(\text{P}-\text{Cl})$, and $^1J(\text{Cl}-\text{Cl})$ for $\text{H}_2\text{XP}:\text{Cl}_2$ complexes with traditional halogen bonds are also reported in Table 10. In contrast to the complexes with chlorine-shared

halogen bonds, these coupling constants exhibit the anticipated distance dependencies. The excellent linear correlation between $^{2X}J(\text{P}-\text{Cl})$ and the distance between P and the distal Cl can be seen in Figure 7. Since the binding energies of these complexes

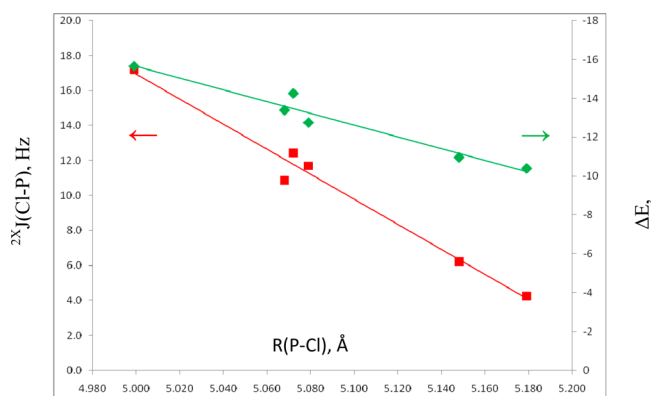


Figure 7. Coupling constants $^{2X}J(\text{Cl}-\text{P})$ (red ■) and binding energies (ΔE , green ◆) versus the distance between P and the distal Cl for complexes $\text{H}_2\text{XP}:\text{Cl}_2$ with traditional halogen bonds. The correlation coefficients R^2 are 0.980 and 0.949, respectively.

also depend on this same distance, a plot of this variable has also been included in Figure 7. $^{2X}J(\text{P}-\text{Cl})$ also correlates with the distance between P and the proximal Cl, and with the $\text{Cl}-\text{Cl}$ distance, with correlation coefficients of 0.983 and 0.991, respectively. $^{2X}J(\text{P}-\text{Cl})$ values for these complexes are significantly smaller than $^{2X}J(\text{P}-\text{Cl})$ for complexes with chlorine-shared halogen bonds. This reflects the different nature of the halogen bonds, and the longer $\text{P}-\text{Cl}$ distances across traditional halogen bonds.

$^1J(\text{P}-\text{Cl})$ values for traditional halogen bonds have a much narrower range than those for complexes with chlorine-shared halogen bonds, varying from 150 Hz for $\text{H}_2(\text{CN})\text{P}:\text{Cl}_2$ to 256 Hz for $\text{H}_2(\text{CCH})\text{P}:\text{Cl}_2$. Although these coupling constants vary with the distances between P and both the proximal and distal Cl atoms, the correlations are not strong, with correlation coefficients between 0.87 and 0.89. Finally, from Table 10 it is apparent that $^1J(\text{Cl}-\text{Cl})$ in $\text{H}_2\text{XP}:\text{Cl}_2$ complexes decreases only by about 2 Hz relative to the monomer value of 99.6 Hz, and varies by only 0.5 Hz in the complexes. With such a small variation, $^1J(\text{Cl}-\text{Cl})$ does not exhibit any mathematically significant relationship with the $\text{P}-\text{Cl}$ or $\text{Cl}-\text{Cl}$ distances.

CONCLUSIONS

Ab initio MP2/aug'-cc-pVTZ calculations have been carried out on complexes $\text{H}_2\text{XP}:\text{ClF}$ and $\text{H}_2\text{XP}:\text{ClCl}$, with $\text{X} = \text{F}, \text{Cl}, \text{OH}, \text{NC}, \text{CN}, \text{CCH}, \text{CH}_3$, and H . The results of these calculations support the following statements.

1. $\text{H}_2\text{XP}:\text{ClF}$ complexes are stabilized by chlorine-shared halogen bonds, with short $\text{P}-\text{Cl}$ and significantly elongated $\text{Cl}-\text{F}$ distances. Their binding energies are high, ranging between -30 and $-93 \text{ kJ}\cdot\text{mol}^{-1}$. The relative binding energies of these complexes can be explained in terms of the stability of the $\text{H}_2\text{XP}:\text{Cl}^+$ cations and the interaction between these cations and F^- .

2. $\text{H}_2(\text{OH})\text{P}:\text{Cl}_2$ and $\text{H}_2(\text{CH}_3)\text{P}:\text{Cl}_2$ complexes are stabilized only by chlorine-shared halogen bonds, while $\text{H}_3\text{P}:\text{Cl}_2$, $\text{H}_2(\text{CN})\text{P}:\text{Cl}_2$, and $\text{H}_2(\text{NC})\text{P}:\text{Cl}_2$ complexes are stabilized only by traditional halogen bonds. In contrast, the potential surfaces of $\text{H}_2\text{FP}:\text{Cl}_2$, $\text{H}_2(\text{CCH})\text{P}:\text{Cl}_2$, and $\text{H}_2\text{ClP}:\text{Cl}_2$ have

double minima along the halogen-bonding coordinate. There is only a small barrier for converting the less stable $\text{H}_2\text{FP}:\text{Cl}_2$ complex with a traditional halogen bond to the more stable chlorine-shared complex. However, on the $\text{H}_2(\text{CCH})\text{P}:\text{Cl}_2$ and $\text{H}_2\text{CIP}:\text{Cl}_2$ surfaces, the less stable chlorine-shared complexes exist in very shallow minima, with extremely small barriers to converting them to traditional halogen-bonded equilibrium structures.

3. There are several factors which determine the binding energies of $\text{H}_2\text{XP}:\text{ClF}$ and $\text{H}_2\text{XP}:\text{ClCl}$ complexes, including the electron-donating ability of H_2XP and the electron accepting ability of ClF and ClCl , the nature of the halogen bond, secondary interactions, and charge-transfer interactions.

4. $\text{P}\cdots\text{Cl}$ bonds with partial covalent character are found for the $\text{H}_2\text{XP}:\text{ClF}$ complexes, and for the $\text{H}_2(\text{OH})\text{P}:\text{ClCl}$ and $\text{H}_2\text{FP}:\text{ClCl}$ complexes with chlorine-shared halogen bonds and the shortest distances between P and the proximal Cl. Relative to these, the remaining $\text{H}_2\text{XP}:\text{ClCl}$ complexes with chlorine-shared halogen bonds have $\text{P}\cdots\text{Cl}$ bonds with reduced covalent character. The traditional $\text{P}\cdots\text{Cl}$ bonds in $\text{H}_2\text{XP}:\text{ClCl}$ complexes have little or no covalency.

5. The changes in the electron populations of ^{31}P , ^{19}F , and ^{35}Cl upon formation of $\text{H}_2\text{XP}:\text{ClY}$ complexes are consistent with electron donation by H_2XP to ClY . However, the changes in these populations do not correlate with the changes in the chemical shieldings of these atoms.

6. For complexes $\text{H}_2\text{XP}:\text{ClF}$, EOM-CCSD coupling constants $^{2X}J(\text{P}-\text{F})$ do not correlate with $\text{P}-\text{F}$, $\text{P}-\text{Cl}$, or $\text{F}-\text{Cl}$ distances. Decreasing $^{1X}J(\text{Cl}-\text{P})$ does correlate with increasing $\text{Cl}-\text{F}$ distance as the values of this coupling constant approach the values of $^1J(\text{Cl}-\text{P})$ for the corresponding cations $\text{H}_2\text{XP}^+\text{Cl}^-$. Although $^1J(\text{F}-\text{Cl})$ does not correlate with the $\text{F}-\text{Cl}$ distance, it does correlate with the $\text{P}-\text{Cl}$ distance. Thus, the distance dependencies or lack of such for these coupling constants are unusual.

7. $^{2X}J(\text{P}-\text{Cl})$ and $^{1X}J(\text{P}-\text{Cl})$ values for $\text{H}_2\text{XP}:\text{ClCl}$ complexes with chlorine-shared halogen bonds do not exhibit strong correlations with $\text{P}-\text{Cl}$ or $\text{Cl}-\text{Cl}$ distances, although $^{1X}J(\text{P}-\text{Cl})$ does correlate with the binding energies of these complexes. Like $^1J(\text{F}-\text{Cl})$ for $\text{H}_2\text{XP}:\text{ClF}$ complexes, $^1J(\text{Cl}-\text{Cl})$ correlates linearly with the distance between P and the proximal Cl. In contrast, $^{2X}J(\text{P}-\text{Cl})$ values for $\text{H}_2\text{XP}:\text{ClCl}$ complexes with traditional halogen bonds correlate with $\text{P}-\text{Cl}$ and $\text{Cl}-\text{Cl}$ distances, and $^{1X}J(\text{P}-\text{Cl})$ shows some correlation with both $\text{P}-\text{Cl}$ distances. There is only a very small variation in $^1J(\text{Cl}-\text{Cl})$ in these complexes, and no distance correlations.

■ ASSOCIATED CONTENT

Supporting Information

Geometries, total energies, and molecular graph for $\text{H}_2\text{XP}:\text{ClF}$ and $\text{H}_2\text{XP}:\text{Cl}_2$ complexes; coupling constants $^{2X}J(\text{P}-\text{F})$, $^{2X}J(\text{P}-\text{Cl})$, $^{1X}J(\text{P}-\text{Cl})$, $^1J(\text{F}-\text{Cl})$, and $^1J(\text{Cl}-\text{Cl})$ and their components for complexes $\text{H}_2\text{XP}:\text{ClF}$ and $\text{H}_2\text{XP}:\text{Cl}_2$, and for the monomers ClF and Cl_2 ; $^1J(\text{P}-\text{Cl})$ and components for cations $\text{H}_2\text{XP}^+\text{Cl}^-$; full references 22 and 39. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: ibon@iqm.csic.es.

*E-mail: jedelbene@ysu.edu.

Notes

The authors declare no competing financial interest.

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