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Singlet Phosphinidene Insertions in H_2O, H_2S, HF, and HCl. Comparisons with Carbene, Nitrene, and Silylene Insertions

Pamidighantam V. Sudhakar and Koop Lammertsma*

Department of Chemistry, University of Alabama at Birmingham, UAB Station, Birmingham, Alabama 35294

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The insertion reaction of phosphinidene ^1PH into H_2O, H_2S, HF, and HCl has been studied by ab initio molecular orbital theory including electron correlation and zero-point energy corrections. Bader's charge density analysis has been used to delineate the bonding in initially formed donor–acceptor complexes, in the transition structures for hydrogen migration, and in the insertion products. Comparisons with the corresponding nitrene, carbene, and silylene insertions are made. Differences in the geometries and the kinetic stabilities of the ylide structures can be attributed to the electronegativity differences of the singlet (^1A) diradical species.

Insertion reactions of singlet (^1A) diradicals are of current interest.[1] Most mechanistic studies, experimental[2] and theoretical,[3] concern the insertion of carbene $^1CH_2$ and silylene $^1SiH_2$. Analogous nitrene (^1NH) reactions have been explored in less detail,[1,4,5] and those of the ^1PH phosphinidene received the least attention. The latter is of significant interest however as illustrated by the exponential growth of the chemistry of phosphinidenes that are stabilized by organometallic π-donor groups.[6,7] For example, the mechanism for alkene (and diene) addition of such complexes (R—P—$W(CO)_5$, R = Ph, OCH_3, NEt_2)[8] has been studied experimentally by Mathey et al.[6a] and theoretically (R = H) by Gonbeau et al.[9] Recently, we determined the Hammett reaction constant for alkene addition of the phosphinidene Ph—P—$W(CO)_5$ and confirmed its electrophilic carbene-like nature[10]—only for some carbenes are ρ values available. Does the uncomplexed parent phosphinidene (^1PH) also display carbene-like characteristics? We decided to investigate by ab initio MO theory the insertion of phosphinidene in X—H bonds (X = O, S, F, Cl), since similar solvent insertion studies have been reported for $^1CH_2$,[3h] $^1SiH_2$,[3f] and ^1NH.[5] These studies unequivocally illustrated the presence of solvent addition complexes prior to insertion. Such solvent complexes can display high stabilities as was illustrated in our recent theoretical study on nitrene insertions.[5] We also showed[11] that the nitrene–phosphine species, the parent Staudinger complex, is a tightly bound ylide ($H_3P^+—^-NH$) similar to the Wittig reagent $H_3P^+—^-CH_2$. In contrast, the NPH_4 isomeric phosphinidene–ammonia complex, which is nearly isoenergetic with the Staudinger complex, was shown to display only van der Waals interactions.[11] This, of course, focuses on the difference between N and P ligand interactions and possibly on the phosphorus valency.[12] Interestingly, however, Francl et al.[13] in a theoretical study suggested similar zwitterionic character for the PC bond in both the trivalent HP=CH_2 and the "pentavalent" H_3P=CH_2.

Phenyl phosphinidenes (Ph—P) are known to insert into single bonds to yield X—PPh—Y products. Such insertions have been reported for the C—C bonds of biphenylenes,[14] the C—S bonds of allyl sulfides,[15] the S—S bonds of disulfides,[16] and for As—As bonds.[17] Various isomers of RPX_2 have been synthesized[18] (R = H, Cl; X_2 = ethylene,[18b] O_2,[18c,d] S_2,[e,f] Se_2[18g]) and studied by theory.[19] For the oxygen and sulfur derivatives of HPX_2 the stability order was calculated as phosphine (X=P—XH) < bisphosphorane (X=PH=X, an X_2 insertion product) <

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Table I. Total (au) and Relative (kcal/mol) Energies of Singlet Phosphinidene Complexes with H_2O, H_2S, HF, and HCl

structure		state	HF/3-21G total	HF/3-21G rel	HF/6-31G* total	HF/6-31G* rel	MP2(Full)/6-31G* total	MP2(Full)/6-31G* rel	MP2(Full)/6-31G* NIMAG	MP4(FC)/6-311G**[a] total	MP4(FC)/6-311G**[a] rel	Corr MP4[a,b] rel
1	C_s	$^1A'$	−415.15477	0.0	−417.31424	0.0	−417.61072	0.0	(0)	−417.72789	0.0	0.0
2	C_s	$^1A'$	−415.11815	23.0	−417.23160	51.9	−417.52495	52.5	(0)	−417.64722	50.6	51.2
3	C_1	^1A	−415.04920	66.3	−417.18182	83.1	−417.50252	67.9	(1)	−417.62489	64.6	60.3
4	C_s	$^1A'$	−736.27516	0.0	−739.97316	0.0	−740.21429	0.0	(0)	−740.32736	0.0	0.0
5	C_s	$^1A'$	−736.20906	41.8	−739.89073	51.7	−740.13521	49.6	(0)	−740.25029	48.4	48.3
6	C_1	^1A	−736.17796	61.0	−739.85469	74.3	−740.10493	68.6	(1)	−740.22831	62.2	60.0
7	C_s	$^1A'$	−439.16500	0.0	−441.32019	0.0	−441.60702	0.0	(0)	−441.72934	0.0	0.0
8	C_1	^1A	−438.96480	125.6	−441.20586	71.7	−441.48739	75.1	(0)	−441.62036	68.4	67.1
9	C_1	^1A	−438.92083	153.2	−441.17527	90.9	−441.48101	93.4	(1)	−441.61227	73.5	70.5
10	C_s	$^1A'$	−797.44078	0.0	−801.36887	0.0	−801.61753	0.0	(0)	−801.71699	0.0	0.0
11	C_1	^1A	−797.35917	51.2	−801.25702	70.2	−801.50022	73.6	(0)	−801.60803	68.4	66.9
12	C_1	^1A	−797.33887	64.0	−801.23800	82.1	−801.49102	79.4	(1)	−801.60317	71.4	68.4

[a] Based on MP2/6-31G* optimized geometries. [b] Corrected for zero point energies, scaled by 0.95.

Table II. The MP2/6-31G* Vibrational Frequencies (in cm^{-1}) for ^1PH complexes with H_2O, H_2S, HF, and HCl

geometries		frequencies[a]												
1	C_s	273	(a″,110)	816	(a′,107)	945	(a′,20)	946	(a″,2)	1199	(a′,39)	1205	(a′,151)	
		2496	(a′,110)	2498	(a″,148)	3810	(a′,103)							20.3
2	C_s	264	(a″,70)	415	(a′,73)	628	(a′,219)	715	(a″,2)	857	(a′,54)	1690	(a′,102)	
		2483	(a′,158)	3720	(a′,153)	3845	(a″,200)							20.9
3	C_1	1575i	(1394)	503	(105)	535	(89)	782	(20)	995	(79)	1401	(54)	
		1966	(7)	2514	(105)	3690	(121)							17.7
4	C_s	220	(a″,35)	514	(a′,16)	788	(a′,16)	847	(a″,3)	990	(a′,10)	1190	(a′,32)	
		2513	(a′,64)	2519	(a″,80)	2792	(a′,5)							17.7
5	C_s	270	(a″,7)	424	(a′,8)	720	(a′,21)	793	(a″,12)	958	(a′,16)	1349	(a′,106)	
		2479	(a′,113)	2656	(a″,9)	2679	(a′,92)							17.6
6	C_1	946i	(865)	199	(23)	305	(40)	597	(8)	903	(12)	1233	(6)	
		2303	(118)	2457	(125)	2804	(3)							15.4
7	C_s	853	(a′,96)	939	(a″,13)	1020	(a′,62)	1185	(a′,49)	2484	(a′,112)	2494	(a″,166)	12.8
8	C_1	284	(35)	317	(117)	528	(279)	702	(13)	2476	(154)	3878	(245)	11.7
9	C_1	1039i	(1135)	460	(242)	750	(14)	815	(53)	2290	(112)	2496	(120)	9.7
10	C_s	530	(a′,54)	864	(a″,5)	921	(a′,41)	1167	(a′,26)	2500	(a′,70)	2513	(a″,93)	12.1
11	C_1	203	(20)	351	(35)	587	(9)	779	(5)	2468	(146)	2942	(26)	10.5
12	C_1	668i	(612)	187	(79)	453	(19)	667	(2)	2469	(168)	2484	(121)	9.0

[a] Symmetries and intensities are given in parentheses.

phosphirane ($\overline{\mathrm{HPXX}}$, and X_2 addition product),[19a] while in the case of X = CH_2 (and SiH_2) the phosphirane is much more stable than the bisphosphorane $H_2C{=}PH{=}CH_2$.[19b] Mathieu et al.[19a] have suggested that the strong P—X bond in the latter bisylide structure results from hypervalent stabilizations, which concurs with the phosphorus d orbital participation suggested by Dobbs et al.[19b]

Some trends have emerged from the earlier theoretical studies on the carbene, nitrene, and silylene insertions into solvent molecules. First-row hydrides (CH_4, NH_3, OH_2) appear to complex better with second row singlet ^1A diradicals than with the first-row species and the opposite applies to second-row hydrides (SiH_4, PH_3, SH_2) but less pronounced. Further, nitrene complexes have higher barriers for hydrogen migration (to yield insertion products) than their carbene analogues (except for the HF complex). The present investigation aims to fill a void in exploring the corresponding phosphinidene addition complexes and insertions into the X-H bond of solvent molecules (X = O, S, F, Cl). In addition, we report on the nature of the interaction between phosphinidene ^1PH and the solvent molecules.

Methods

Ab initio molecular orbital calculations[20] were carried out using the GAUSSIAN 88[21] series of programs. Geometries were optimized within indicated symmetries using the split-valence 3-21G[22] and d-polarized 6-31G*[23] basis sets within the restricted Hartree–Fock approximation. All electron correlation effects on the geometry were evaluated, using Møller–Plesset perturbation theory[24] at second order; these are important when electronegative elements are involved in weak bonding interactions. Energy evaluations were performed at MP4(FC)/6-311G** + scaled[25] zero-point energies (ZPE), which include correlation of valence electrons up to full fourth-order terms using a triply split valence shell with p- and d-polarization functions for hydrogen and non-hydrogen atoms,[26] respectively.

The nature of bonding in the MP2(Full)/6-31G* optimized geometries was investigated using the correlated one-electron density distributions with Bader's topological theory of atoms in molecules.[27,28] The (3,−1) or "bond critical points" $\mathbf{r}_b$, which

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Table III. MP4/6-311G Binding Energies (in kcal/mol) of PXH_n (X = O, S, F, Cl)[a]**

2	→	$OH_2 + PH$	21.0
5	→	$SH_2 + PH$	25.9
8	→	$FH + PH$	7.0
11	→	$ClH + PH$	6.0
1	→	$OH_2 + PH$	72.3
4	→	$SH_2 + PH$	74.2
7	→	$FH + PH$	74.4
10	→	$ClH + PH$	72.9

[a] Corrected for 0.95 scaled ZPEs.

have a minimum value in $\rho(\mathbf{r})$ along the maximum electron density path connecting two nuclei were located. The magnitude of the soft curvature $\lambda_2(\mathbf{r})$ of the three eigenvalues of the Hessian of $\rho(\mathbf{r})$ at a bond critical point characterizes the topological stability of a structure. The Laplacian of the $\rho(\mathbf{r})$ shows regions in space where charge is relatively concentrated ($\nabla^2\rho(\mathbf{r}) < 0$) or depleted ($\nabla^2\rho(\mathbf{r}) > 0$). $H(\mathbf{r})$, the sum of the potential and kinetic energy density terms leading to local total energy density at a (3,−1) critical point, gives an indication of the nature of the bond.[29]

Results and Discussion

The MP2 and HF/6-31G* (in parentheses) optimized geometries of the ^1PH-complexes with H_2O, H_2S, HF, and HCl, their tautomers, and the corresponding transition structures for hydrogen migration are given in Figure 1. Their energies at various levels of theory are listed in Table I. This table also gives the number of imaginary MP2/6-31G* frequencies (NIMAG), which serves to characterize minima (NIMAG = 0) and transition structures (NIMAG = 1); the harmonic vibrational frequencies are listed in Table II. The final column in Table I gives the relative energies at MP4(FC)/6-311G** + scaled ZPE. These energies are used throughout the text. Figure 1 and Table I also display the sensitivity of geometries and energies to the theoretical levels employed. Binding energies are listed in Table III. The MP2/6-31G* bond critical point data of structures **1**–**12** are given in Table IV.

Structures and Energies. Complexes of the singlet nitrene, carbene, and silylene with water have been inferred in earlier studies,[3] which leads to the expectation that phosphinidene too will render a complex with water. This and the complex with H_2S are confirmed. While the HP—OH_2 isomer **2** is a large 51.2 kcal/mol less stable than hydroxyphosphine H_2P—OH (**1**) it has a barrier of 9.1 kcal/mol for hydrogen migration via **3** and a binding energy of 21.0 kcal/mol. The P—O bond of 2.013 Å in **2** is much longer (0.332 Å) than in its tautomer **1**. This and the less than orthogonal HPO angle[30] suggest **2** to be a van der Waals or donor–acceptor complex between ^1PH and H_2O. In the transition structure **3** the distance between the P and O atoms decreases with both sharing a hydrogen, which is indicative of an interaction between an O—H bond and the empty p orbital. Structure **2** may be compared with the ^1PH–ammonia complex, which also represents a van der Waals complex but has a higher barrier (26.5 kcal/mol, MP4/6-31G* + ZPE) for hydrogen migration.[11] The rearrangement barrier appears unexpectedly similar to the 6.9 kcal/mol for the nitrene–water complex (which has a much earlier transition),[5] since the silylene O—H insertion barrier of 38 kcal/mol is much larger than the ca. 1 kcal/mol for the carbene–water complex.[3h]

Table IV. MP2/6-31G* Bond Critical Point Data for PXH_n Species (X = O, S, F, Cl; n = 1, 2)[a]

struct	bond X—Y	d_x	d_y	ϵ	$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	$H(\mathbf{r})$
1	P—O	0.655	1.028	0.026	0.978	13.894	−0.611
	O—H	0.777	0.193	0.016	2.268	−41.776	−3.411
	P—H	0.693	0.723	0.203	1.113	−4.381	−1.171
2	P—O	0.856	1.170	1.378	0.457	2.097	−0.219
	O—H	0.789	0.186	0.017	2.228	−43.276	−3.446
	P—H	0.703	0.716	0.614	1.068	−3.933	−1.088
3	P—H_1	1.080	0.576	0.856	0.607	0.423	−0.243
	O—H_1	0.887	0.287	0.102	1.274	−10.187	−1.322
	O—H_2	0.788	0.193	0.005	2.204	−40.597	−3.289
	P—H_3	0.701	0.714	0.433	1.092	−4.384	−1.131
4	P—S	0.918	1.210	0.013	0.842	−4.571	−0.564
	S—H	0.870	0.471	0.087	1.388	−12.129	−1.149
	P—H	0.696	0.718	0.144	1.103	−4.185	−1.151
5	P—S	0.804	1.337	0.959	0.684	−0.568	−0.505
	S—H	0.889	0.461	0.062	1.404	−12.675	−1.144
	P—H	0.703	0.716	0.417	1.063	−3.547	−1.082
6	P—S	1.055	1.348	0.406	0.428	0.443	−0.147
	S—H_2	0.881	0.459	0.033	1.408	−12.700	−1.162
	S—H_1	0.950	0.437	0.492	1.057	−4.068	−1.075
	P—H_3	0.707	0.716	0.076	1.249	−9.291	−0.907
7	P—F	0.650	0.977	0.084	0.943	18.340	−0.475
	P—H	0.696	0.724	0.221	1.120	−5.053	−1.190
8	P—F	0.989	1.161	0.638	0.320	2.141	−0.105
	P—H	0.706	0.716	0.665	1.074	−4.565	−1.103
	F—H	0.791	0.156	0.003	2.109	−50.069	−3.981
9	P—F	1.039	1.117	13.445	0.490	2.924	−0.170
	F—H	0.851	0.210	0.033	1.497	−16.269	−1.769
	P—H	0.704	0.715	0.535	1.095	−4.914	−1.139
10	P—Cl	0.802	1.272	0.089	0.815	−3.754	−0.672
	P—H	0.697	0.719	0.154	1.117	−4.873	−1.179
11	P—Cl	1.010	1.362	0.688	0.365	1.447	−0.115
	P—H	0.706	0.716	0.596	1.069	−4.324	−1.094
	Cl—H	0.922	0.367	0.017	1.556	−16.185	−1.439
12	P—Cl	1.152	1.407	1.451	0.249	1.828	−0.029
	P—H	0.707	0.714	0.576	1.082	−4.945	−1.120
	Cl—H	0.366	0.958	0.004	1.388	−12.590	−1.194

[a] d_x(d_y) is the distance from the critical point to atom X (Y); $\rho(\mathbf{r})$ is in e A^{-3}; $\nabla^2\rho(\mathbf{r})$ is in e A^{-5}; $H(\mathbf{r})$ is in Hartree A^{-3}.

The heavier PSH_4 system appears much the same as the lighter OPH_4. Thus, the HP—SH_2 complex **5**, with a binding energy of 25.9 kcal/mol, is also much less stable (48.3 kcal/mol) than its thiolphosphine tautomer H_2P—SH (**4**) with a similar barrier for hydrogen migration (11.7 kcal/mol via **6**). It is then suprising that the P—S distances in **5** (2.135 Å) and **4** (2.127 Å) are virtually the same. This is in sharp contrast with the corresponding NSH_4 isomers, of which sulfilimine HN—SH_2 has a 1.597 Å N—S bond length that is 0.134 Å shorter than in the 49.3 kcal/mol more stable thiamine,[5] but similar to the analogous P_2H_4 isomers, of which HP—PH_3 and H_2P—PH_2 have P—P bonds of similar lengths.[11] Common to the PSH_4 and P_2H_4 system is that both contain two second-row elements. Very recently the parent H_2P—SH species **4** has been observed by neutralization reionization mass spectrometry.[31]

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[28] The programs SADDLE and PROAIM, provided by Professor R. F. W. Bader, were used to evaluate the topological properties of the electron densities. The algorithm is described in: Biegler-König, F. W.; Bader, R. F. W.; Tang, T.-H. *J. Comput. Chem.* **1982**, *3*, 317.

[29] Cremer, D.; Kraka, E. *Croat. Chim. Acta* **1984**, *57*, 1259.

[30] Orthogonal angles at P centers are much more common than those at C, N, and O centers: Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.

[31] (a) Heck, H.; Kuchen, W.; Rennenberg, H.; Terlouw, J. K. *Phosphorus Sulfur Silicon Relat. Elem.* **1990**, *51/52*, 182. (b) Heck, H.; Kuchen, W.; Rennenberg, H.; Terlouw, J. K. *Phosphorous Sulfur Relat. Elem.* **1988**, *40*, 227.

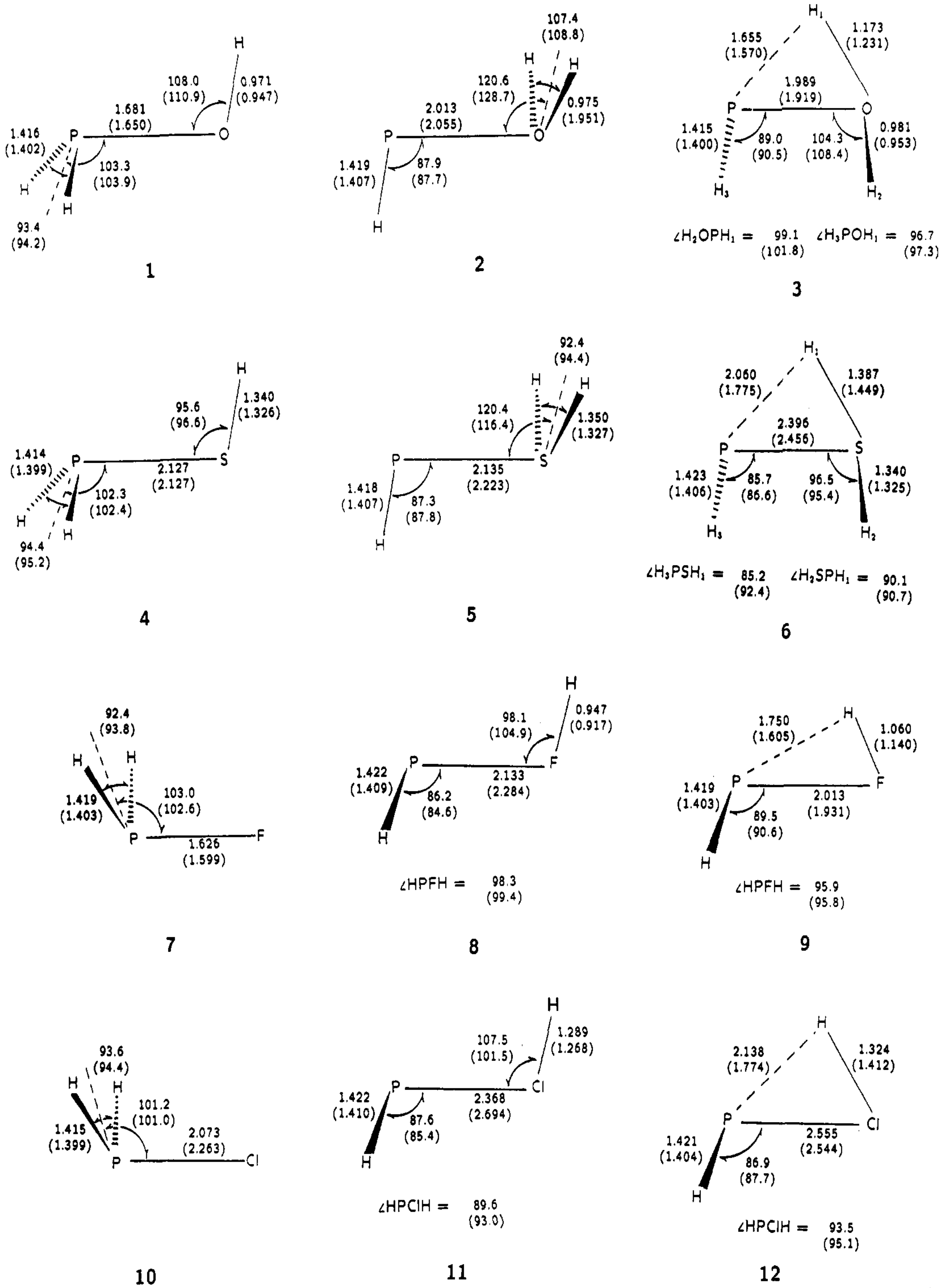

Figure 1. MP2/6-31G* optimized structures for 1–11. HF parameters are given in parentheses.

The ^{1}PH insertion into hydrogen halide bonds shows similarities with the insertions in the O—H and S—H bonds, but differs from the corresponding nitrene insertions. While ^{1}NH inserts in HF without barrier to give fluoroamine,[5] the phosphinidene complex **8** has a small barrier (via **9**) of 3.4 kcal/mol to yield the 67.1 kcal/mol more stable fluorophosphine H_2P—F (**7**). The 2.133 Å P—F bond length of **8** reduces significantly (0.507 Å) in this process and suggests that HP—FH (**8**) represents a van der Waals complex. The particularly high sensitivity of the relative energies to the theoretical levels in this PFH_2 system is noted.

Expectantly, ^{1}PH also complexes with HCl to yield **11**. The barrier (via **12**) of only 1.6 kcal/mol for rearrangement to the 66.9 kcal/mol more stable chlorophosphine H_2P—Cl (**10**), however, is surprisingly similar to the insertion into HF. The P—Cl bond length of 2.368 Å for **11** is also long. In contrast, the nitrene complex of HCl has a N—Cl bond length (1.678 Å) that is much shorter than in chloramine.

It is evident that the considered ^{1}PH reactions give complexes before formation of the thermodynamically much more stable insertion products, the magnitude of which is sensitive to the theoretical level employed. The initial complexes with H_2O, H_2S, HF, and HCl all seem to represent van der Waals interactions, whereas the ^{1}NH complexes of H_3P (Staudinger), H_2S (sulfilimine), and HCl all display strong ylide behavior.[5,11] Because stabilization has also been ascribed to the HP—PH_3 species[11] it is relevant to investigate in more detail the bonding properties of the addition complexes.

Electron Densities. It is evident from Table IV that the ^{1}PH complexes of H_2O **2**, HF **8**, and HCl **11** represent weak van der Waals interactions or Lewis donor-acceptor complexes. The electron density ρ, the Laplacian $\nabla^2\rho(\mathbf{r}_{b1})$, and the total energy density H of the P—X (X = O, F, Cl) bond critical point for these species are much smaller than in their more stable tautomers. This is highlighted in the transition structure **3** for the phosphinidene-water insertion that does not even possess a P—O bond path. The three complexes **2**, **8**, and **11** also have rather high P—O bond ellipticities, which is not common for covalent bonds.

The characteristics of the HP—SH_2 complex **5** are somewhat different from the others. The magnitude of both the electron density ρ and the total energy density H at its P—S bond critical point are only slightly less than those of the more stable tautomer **4**, while its ϵ value is much higher. This behavior of **5** shows similarities with the HP—PH_3 structure,[11] in which case the effects are even more pronounced. For example, the 2.087 Å P—P bond of HP—PH_3 is 0.123 Å shorter than that of diphosphine, while the P—S bond of 2.135 Å in **5** is 0.008 Å longer than that of **4**. It appears that the ylide character of the ^{1}PH complexes of the second-row hydrides diminishes from PH_3, via SH_2 to HCl, where it is no longer detected. The electron density of the respective bond critical points in this series decreases, indicating a reduction of electron transfer between the heavy elements. This may be a result of the balance of the elemental electronegativities. While corresponding nitrene complexes have been shown to possess a much stronger ylide character, those (^{1}NH) of the first-row hydrides also do not display any significant charge transfer.

Molecular Orbitals. The geometrical parameters and the electron density properties suggest that with the possible exception of **5** none of the ^{1}PH complexes of this study experience increased bonding. Indeed they lack negative hyperconjugative stabilization. Only the HOMO of HP—SH_2 shows a hyperconjugative interaction between the lone pair on the phosphorus and the π^* orbital of the SH_2 group. The HOMO of the other complexes comprises of a P lone pair. For all (**2**, **5**, **8**, and **11**) the LUMO is a PX (X = O, S, F, Cl) σ^* orbital with a minor X—H antibonding contribution. The HOMO-1 and -2 for **2** and **5** are combinations of P—H and P—X bonding orbitals, whereas in **8** and **11** they represent P—H σ-bonding and an X lone pair, respectively. None of the complexes show any significant d participation of the phosphorus atom in line with the recognized absence of P hypervalency in many hypercoordinated systems.[12] Electron-withdrawing substituents (like F) on both the heteroatoms and phosphorus should stabilize the phosphinidene complexes through increased negative hyperconjugation and lone-pair delocalization, respectively.

Conclusions and Comparisons

Singlet phosphinidene ^{1}PH gives addition complexes with H_2O, H_2S, HF, HCl, and as we have shown earlier[11] also with H_3N and H_3P prior to insertion to yield the more stable tautomers. The overall process for ^{1}PH insertion into the solvent molecules of this study occurs with a negative activation energy. The initial interaction between ^{1}PH and the solvents are best described as van der Waals or donor-acceptor complexes. These have small barriers for hydrogen migration to the thermodynamically much more stable substituted phosphines. None of the complexes show any P hypervalency or d orbital participation. Only the HP—SH_2 complex **5** shows some ylide-like stabilization; it is also the kinetically more stable species.

Trends emerge on comparing singlet phosphinidene complexes with those of $^1CH_2$, $^1SiH_2$, and ^{1}NH. The first-row species $^1CH_2$ and ^{1}NH give very strong bonds (ylides and partially triple bonds) with second-row hydrides. Typical examples are H_3PCH_2 (Wittig), H_3PNH (Staudinger), and H_2SNH (sulfilimines), but also H_3PO and H_2SO (sulfoxides). The main driving force is the charge stabilization in these systems; none of them possesses hypervalent character. Such strong stabilizations occur neither for combinations within the first row nor for combinations within the second row. Within a row the complexation reduces from left to right, thus HP—PH_3 > HP—SH_2 > HP—ClH. Barriers for hydrogen migration are smaller for the ^{1}PH ylides than for the corresponding silicon species. The main factor differentiating the various complexes is the difference in electronegativities of the non-hydrogen atoms. Substitutions by electronegative groups should render complexes that are less prone to rearrangement.

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