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Theoretical Study of the Tautomerism, Structures, and Vibrational Frequencies of the Phosphaalkenes $XP{=}C(CH_3)_2$ ($X = H, F, Cl, Br, OH, Ar_F$ ($Ar_F = 2,6\text{-}(CF_3)_2C_6H_3$))[†]

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Received: September 30, 2008; Revised Manuscript Received: December 23, 2008

Ab initio theoretical calculations have been used to study the influence of phosphorus substituents, Y, on the tautomerism between the vinylphosphine $XP(H)C(CH_3){=}CH_2$ and the phosphaalkene $XP{=}C(CH_3)_2$ ($X = H$, F, Cl, Br, OH, and Ar_F; $Ar_F = 2,6\text{-}(CF_3)_2C_6H_3$) and on the acidity of the aforementioned vinylphosphine. The stabilization of the phosphaalkene and the increased acidity of the vinylphosphine by Ar_F are possible factors in the successful synthesis of certain isolable phosphaalkenes. In this work, the properties of Ar_F are assessed theoretically. Density functional theory using the B3LYP functional has been used for all substituents. In addition, coupled-cluster singles and doubles with noniterative triples (CCSD(T)) has been used for $X = H$, F, Cl, Br, and OH. The phosphaalkene is favored over the vinylphosphine for all substituents, with F having the strongest stabilizing effect. Cl, Br, and OH have stronger stabilizing effects than Ar_F. In contrast, the most acidic vinylphosphine is that with Ar_F. To aid in the interpretation and analysis of future experimental work, CCSD(T) calculations were used to provide structures and vibrational frequencies for the series $XP{=}C(CH_3)_2$ ($X = H$, F, Cl, Br). The influence of the substituent on geometries and C=P and X−P stretching frequencies was examined, and comparisons were made with the $CH_2{=}PX$ series.

Introduction

The chemistry of compounds that contain a carbon−phosphorus double bond, that is, the phosphaalkenes, has advanced considerably.[1−5] These compounds were initially an intellectual curiosity, and the early goals of their study were simply the unequivocal detection of these species. Following spectroscopic characterization of transient prototypes such as $CH_2{=}PH$,[6−9] metal complexes of more kinetically stable phosphaalkenes were prepared and characterized.[10−14] As the field has advanced, applications of phosphaalkenes are also being pursued. These include their use as ligands in transition-metal-catalyzed organic reactions [5,15−20] and as sources for new inorganic polymers.[21−23]

One strategy in the development of new inorganic polymers is to use addition polymerization of P=C bonds, yielding new poly(methylenephosphine)s. One example was reported for $MesP{=}CPh_2$ by Tsang et al.[22] This group wished to extend this work to a wider range of substituents. In particular, they have sought to employ phosphaalkenes that have C-alkyl substituents, especially Me, rather than C-aryl. However, known routes to such phosphaalkenes involved P substituents that were expected to hinder polymerization. Accordingly, they developed a new route to phosphaalkenes of the form $Ar_FP{=}C(R)CH_3$ (where Ar_F is 2,6-bis(trifluoromethyl)phenyl ($2,6\text{-}(CF_3)_2C_6H_3$) or 2,4,6-tris(trifluoromethyl)phenyl ($2,4,6\text{-}(CF_3)_3C_6H_2$) and $R = CH_3$ or C_6H_5).[24] Actually, the route was not fundamentally new, but its application was. Yam et al.[24] considered the known rearrangement of secondary vinylphosphines to phosphaalkenes as a possible pathway: $XP(H)C(Y){=}CH_2 \leftrightarrows XP{=}C(Y)CH_3$. Although this reaction had been used to prepare certain phosphaalkenes,[25,26] it had at the time not been useful for the preparation of *isolable* phosphaalkenes. Cited difficulties included the need to trap phosphaalkenes of low kinetic stability chemically or the production of inseparable mixtures of the secondary vinylphosphine and the corresponding phosphaalkene. It was thought that with an appropriate electron-withdrawing substituent on phosphorus (i.e., Y), the phosphaalkene would be sufficiently stabilized relative to the vinylphosphine so as to make the phosphaalkene isolable. The Ar_F substituents were thought to be suitable choices. Although these substituents had previously been used in low-coordinate phosphorus chemistry, there had been little prior use thereof in phosphaalkene chemistry.[27] Yam et al.[24] were successful in obtaining quantitative conversion of the vinylphosphines to the target phosphaalkenes.

The initial goal of the present research was to make a theoretical investigation of aspects of the formation of phosphaalkenes from vinylphosphines by the 1,3-hydrogen migration described above; in particular, to assess the role of the Ar_F substituents. As mentioned, these were thought to be important for at least two reasons. First, they were expected to favor the phosphaalkene in the tautomerism equilibrium. Second, they might increase the acidity of the P−H group, thus facilitating the base-catalyzed hydrogen shift. We have used ab initio quantum chemical methods to assess the role of the Ar_F substituent. We have done so by (1) calculating the free energy change (and equilibrium constant) of the tautomerization; (2) calculating the deprotonation energy of $CH_2{=}CPHAr_FCH_3$; and (3) comparing the results for Ar_F with those of several other

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[†] Part of the "Max Wolfsberg Festschrift".

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10.1021/jp808638s CCC: $40.75

substituents (H, F, Cl, Br, and OH). The size of Ar_F is such that the most sophisticated quantum chemical methods (e.g. coupled-cluster (CC) methods) are too costly to be applied to the actual compounds used in the experiments.[24] Instead, we have applied density functional theory (DFT) to the Ar_F-substituted compounds. In addition, for the smaller substituents listed in item 3 above, we have used CC methods as well as DFT. These calculations have two roles. First, they enable a comparison of the DFT results with those from the most rigorous single-reference methodology; namely, CC singles and doubles with noniterative triples (CCSD(T)). If the DFT results are in close accord with those of CCSD(T), we will have more confidence in using DFT for larger systems of this general type. Second, they provide a comparison of the effects of Ar_F with those of H, F, Cl, Br, and OH.

A useful byproduct of the work on substituent effects was a set of molecular structures and vibrational frequencies of the series $(CH_3)_2C{=}PX$ (X = H, F, Cl, Br) from the CCSD(T) method. These molecules are of some interest themselves and closely related to several previously observed small phosphaalkenes.[28] Furthermore, there have been very few calculations on phosphaalkenes using CC methods for geometries and vibrational frequencies. Accordingly, we report and analyze structural and selected vibrational data on $(CH_3)_2C{=}PX$ as well as compare with data we have obtained on the parent phosphaethenes, $CH_2{=}PX$.

Computational Details

Calculations were performed with the ACES II[29,30] and Gaussian 03[31] programs. The functional used in the DFT calculations is the B3LYP hybrid functional,[32,33] which is well-established as among the most successful functionals. The CC methods used are singles and doubles (CCSD)[34] and CCSD with noniterative triple excitations (CCSD(T)).[35] CCSD, CCSD(T), and B3LYP geometry optimizations were performed on $XP(H)C(CH_3){=}CH_2$, $XP{=}C(CH_3)_2$, and $[XPC(CH_3){=}CH_2]^-$ (X = H, F, Cl, Br, OH) using the 6-311G** and 6-311++G** basis sets.[36−38] Harmonic vibrational frequencies were calculated with CCSD and B3LYP. CCSD(T) frequencies were also calculated for the phosphaalkenes mentioned above. B3LYP geometry optimizations and harmonic frequency calculations were performed on $Ar_FP(H)C(CH_3){=}CH_2$, $Ar_FP{=}C(CH_3)_2$, and $[Ar_FPC(CH_3){=}CH_2]^-$ (Ar_F = 2,6-bis(trifluoromethyl)phenyl), also with the 6-311G** and 6-311++G** basis sets. The harmonic vibrational frequencies have several uses: (1) to determine whether the stationary points were local minima; (2) to provide thermal corrections to the 0 K ab initio energies so as to obtain $\Delta H°$, $\Delta S°$, and $\Delta G°$ at room temperature; and (3) to be of assistance in assigning transitions in vibrational spectroscopy. The thermal corrections were calculated using the ideal gas, rigid rotor, and harmonic oscillator approximations. In all calculations, real spherical harmonic d functions were used. Core electrons (1s for C, O, and F; 1s2s2p for P and Cl; 1s2s2p3s3p3d for Br) were not correlated in the CCSD and CCSD(T) calculations. As long as multireference effects are not significant, the CCSD(T) method is expected to provide an excellent estimate of the correlation energy and, consequently, structures, vibrational frequencies, and energetic data of high accuracy.[39−41] For the systems studied, all cluster amplitudes are less than 0.1, implying the insignificance of multireference effects. Hence, the CCSD(T) results are expected to be very reliable and, thus, have predictive value and provide a good benchmark for the B3LYP results.

TABLE 1: CCSD/6-311G and CCSD/6-311++G** Reaction Energies, Enthalpies, Entropies, Free Energies, and Equilibrium Constants for $XP(H)C(CH_3){=}CH_2 \leftrightarrows XP{=}C(CH_3)_2$[a]**

X	ΔE (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1}K^{-1})	$\Delta G°$ (kJ mol^{-1})	K
H	−17.22	−10.47	−3.51	−9.42	4.47×10^1
F	−35.21	−28.93	−4.72	−27.53	6.64×10^4
Cl	−31.17	−25.17	−0.29	−25.08	2.48×10^4
Br	−29.23	−22.99	0.96	−23.27	1.19×10^4
OH	−24.22	−18.58	8.00	−20.96	4.71×10^3
H	−15.79	−9.02	−2.65	−8.23	2.77×10^1
F	−35.41	−29.57	−2.63	−28.79	1.11×10^5
Cl	−29.62	−23.72	1.06	−24.04	1.63×10^4
Br	−27.98	−21.72	2.58	−22.48	8.69×10^3
OH	−28.82	−22.89	4.43	−24.22	1.75×10^4

[a] $\Delta H°$, $\Delta S°$, $\Delta G°$, and K refer to 298.15 K. The first five lines of data are for the 6-311G** basis set; the second five lines are for the 6-311++G** basis set.

TABLE 2: Calculated Energy Differences (ΔE in Units of kJ mol^{-1}) for the Equilibrium $XP(H)C(CH_3){=}CH_2 \leftrightarrows XP{=}C(CH_3)_2$

X	CCSD/ 6-311G**	CCSD(T)/ 6-311G**	CCSD/ 6-311++G**	CCSD(T)/ 6-311++G**
H	−17.22	−20.32	−15.79	−18.88
F	−35.21	−38.51	−35.41	−39.34
Cl	−31.17	−34.72	−29.62	−33.12
Br	−29.23	−32.89	−27.98	−31.62
OH	−24.22	−27.51	−28.82	−32.29

Results and Discussion

Tautomerism. The CCSD/6-311G** and CCSD/6-311++G** values of ΔE, ΔH°, $\Delta S°$, $\Delta G°$, and K for the tautomerism are shown in Table 1. For all substituents, the phosphaalkene is favored. It is most strongly favored for X = F and least favored for X = H. Comparing the results from the two basis sets, one can assess the effect of diffuse functions. For X = H, F, Cl, and Br, diffuse functions increase ΔE, $\Delta H°$, and $\Delta G°$ by less than 2 kJ mol^{-1}. The effect for X = OH is larger (namely, about 4 kJ mol^{-1}) and in the opposite direction. At 298.15 K, $\Delta G°$ is dominated by $\Delta H°$, with little effect (in most cases, <10%) from $T\Delta S°$. For the halogen and OH substituents, the values of K suggest that the equilibrium concentration of the phosphaalkene is over 8000 times that of the vinylphosphine. These results apply, of course, to isolated gas-phase species, and they may be influenced by different solvation effects in solution. In addition, K is very sensitive to $\Delta G°$, a change of 1 kJ mol^{-1} at 298.15 K affecting K by a factor of 1.5.

The effect of connected triple excitations on ΔE can be seen in Table 2, in which CCSD and CCSD(T) results are compared. In all cases, including triple excitations lowers the ΔE by 3−4 kJ mol^{-1}. One would anticipate about the same effect on $\Delta G°$, implying an increase in the CCSD equilibrium constants by more than a factor of 3 (at 298.15 K).

The tautomerism for X = H has also been investigated by Chuang and Lien.[42] They also find the phosphaalkene to be more stable and report a $G2$ value of −2.80 kcal mol^{-1}; that is, −11.7 kJ mol^{-1}. This number apparently is an estimate of the $\Delta H°$ at 0 K and is thus consistent with our results: our CCSD/6-311++G** $\Delta H°$ is −9.02 kJ mol^{-1} (Table 1), which should decrease by ≈3 kJ mol^{-1} when triple excitations are included (Table 2).

The B3LYP results are now considered. The B3LYP/6-311G** and B3LYP/6-311++G** values of ΔE, $\Delta H°$, $\Delta S°$,

TABLE 3: B3LYP/6-311G and B3LYP/6-311++G** Reaction Energies, Enthalpies, Entropies, Free Energies, and Equilibrium Constants for $XP(H)C(CH_3){=}CH_2 \leftrightarrows XP{=}C(CH_3)_2$[a]**

X	ΔE (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1}K^{-1})	$\Delta G°$ (kJ mol^{-1})	K
H	−15.32	−9.01	−2.65	−8.22	2.76×10^1
F	−37.70	−31.18	−5.56	−29.53	1.49×10^5
Cl	−33.22	−27.42	−1.99	−26.83	5.01×10^4
Br	−31.15	−25.22	−1.14	−24.88	2.29×10^4
OH	−28.41	−22.12	3.14	−23.06	1.10×10^4
Ar_F	−23.01	−17.97	3.62	−19.05	2.17×10^3
H	−13.44	−7.14	−2.54	−6.38	1.31×10^1
F	−37.06	−30.50	−5.13	−28.97	1.19×10^5
Cl	−32.60	−26.77	−1.71	−26.26	3.99×10^4
Br	−30.25	−24.29	−1.08	−23.97	1.58×10^4
OH	−32.54	−26.06	2.56	−26.82	5.01×10^4
Ar_F	−24.24	−19.02	2.77	−19.85	3.00×10^3

[a] $\Delta H°$, $\Delta S°$, $\Delta G°$, and K refer to 298.15 K. The first six lines of data are for the 6-311G** basis set; the second six lines are for the 6-311++G** basis set.

TABLE 4: Calculated Energy Differences (kJ mol^{-1}) for the Process $XP(H)C(CH_3){=}CH_2 \rightarrow [XPC(CH_3){=}CH_2)]^- + H^+$

X	B3LYP/ 6-311++G**	CCSD/ 6-311++G**	CCSD(T)/ 6-311++G**
H	1527	1560	1554
F	1504	1541	1533
Cl	1474	1511	1506
Br	1468	1501	1497
OH	1529	1564	1556
Ar_F	1461		

TABLE 5: Calculated Geometric Parameters for $XP{=}C(CH_3)_2$ from the HF/6-311+G(d,p)[a], B3LYP/6-311++G, CCSD/6-311++G**, and CCSD(T)/6-311++G** Methods[b]**

	bond lengths (Å)				bond angles (°)		
	P=C	C−C^1	C−C^2	P−X	XPC	C^{1}CP	C^{2}CP
H	1.669	1.506	1.510	1.409	98.9	126.6	119.4
	1.690	1.504	1.508	1.430	97.6	126.5	118.9
	1.687	1.511	1.515	1.422	97.2	126.6	119.5
	1.696	1.514	1.517	1.424	96.8	126.5	119.4
F	1.647	1.505	1.511	1.608	103.9	126.4	117.6
	1.672	1.500	1.509	1.657	103.2	126.3	116.6
	1.668	1.508	1.515	1.642	102.8	126.8	117.1
	1.678	1.510	1.518	1.648	102.7	126.7	117.0
Cl	1.658	1.502	1.515	2.086	105.6	130.2	115.2
	1.679	1.498	1.512	2.123	105.1	129.7	114.5
	1.675	1.506	1.519	2.095	104.2	130.1	115.1
	1.685	1.508	1.520	2.100	104.1	129.9	115.0
Br	1.659	1.502	1.515	2.247	106.0	130.4	115.0
	1.680	1.497	1.514	2.290	105.9	130.3	114.2
	1.677	1.506	1.520	2.270	105.0	130.8	114.7
	1.687	1.508	1.522	2.274	104.7	130.6	114.7
OH	1.647	1.505	1.511	1.651	104.1	126.5	117.8
	1.672	1.501	1.508	1.688	102.8	126.0	117.1
	1.669	1.509	1.515	1.677	102.4	126.3	117.7
	1.678	1.511	1.517	1.684	102.1	126.2	117.6

[a] The HF data are from reference 43; the other data are from this work. [b] C^1 and C^2 are trans and cis to X, respectively. For each substituent, the rows of data are in the order HF, B3LYP, CCSD, and CCSD(T).

$\Delta G°$ and K for the tautomerism are shown in Table 3. The trends observed for CCSD and CCSD(T) are also apparent in the B3LYP results. Specifically, the phosphaalkene is favored in all cases, and it is most strongly favored for X = F and least favored for X = H. Looking more closely, for the 6-311G** basis set, most of the B3LYP values of ΔE, $\Delta H°$,and $\Delta G°$ are within 2 kJ mol^{-1} of the corresponding CCSD values, and the largest deviation is 2.5 kJ mol^{-1}. The *relative* differences in $\Delta S°$ are much larger, but the B3LYP and CCSD $\Delta G°$ values are nevertheless very close. The differences between CCSD and B3LYP with the 6-311++G** basis set are slightly larger than for the 6-311G** basis set, but the largest difference for $\Delta G°$ is less than 3 kJ mol^{-1}.

B3LYP gives lower (i.e., more negative) values of $\Delta G°$ than CCSD when X is a halogen or OH, but the reverse is true for X = H. Considering that CCSD(T) should give a lower $\Delta G°$ than CCSD, the B3LYP values of $\Delta G°$ are between the CCSD and CCSD(T) values for the halogens and OH. The same is true for ΔE, $\Delta H°$, and K. Overall, then, it appears that the B3LYP description of the tautomerism is quite satisfactory, giving one confidence in applying this method to larger related systems for which CC calculations are not computationally feasible.

Table 3 shows the B3LYP/6-311G** and B3LYP/6-311++G** results for the Ar_F substituent. The stabilizing effect of X = Ar_F is somewhat less than that of the halogens, although substantially larger than for X = H. The $\Delta G°$ for X = Ar_F is more than twice the value for X = H. The extra stabilization of Ar_F over H leads to an equilibrium constant that is a factor of 79 (6-311G**) or 229 (6-311++G**) larger for X = Ar_F and a strongly product-favored equilibrium. These results confirm one of the effects anticipated for the Ar_F substituent.[24]

Substituent Effects on the Acidity of $XP(H)C(CH_3){=}CH_2$. The deprotonation energies for $XP(H)C(CH_3){=}CH_2$ are shown in Table 4. These are the differences between the energies of the vinylphosphine and the anion obtained by deprotonating the vinylphosphine, both structures having been fully optimized. The substituent effects for the deprotonation energies are somewhat different than for the tautomerism. Looking first at the B3LYP/6-311++G** results, one can see that all the halogens increase the acidity relative to H; that is, the deprotonation energies are smaller. The acidity for X = Br is slightly greater than for X = Cl, and both are significantly larger than for X = F. This order, of course, parallels the acidity of HX. The weakest acid is for X = OH. More acidic than any of the halogens is Ar_F. This is an interesting contrast with the results for the tautomerism, for which the phosphaalkene stabilization by the halogens is larger. Of course, it must be remembered that the present results are for isolated (i.e., gas-phase) species, and the effects of solvation are not clear. Nevertheless, the present calculations allow an assessment of the fundamental stereoelectronic factors on the *intrinsic* acidity of the vinylphosphines. According to these factors, Ar_F creates the most acidic hydrogen.

Next, we can judge the B3LYP results for H and the halogens against the CCSD and CCSD(T) deprotonation energies. One sees clearly the parallels between the results. The trends are the same. Furthermore, the relative deprotonation energies are very close. The differences between the "absolute" deprotonation energies are ~30 kJ mol^{-1}, although this is a small percentage (~2%) of the values. The consistency between the B3LYP and CC results gives further support to the predictions of B3LYP as to the effect of Ar_F on acidity.

Molecular Structures. Table 5 shows the bond lengths and bond angles around the P=C core calculated with several methods and the 6-311++G** basis set for the series $XP{=}C(CH_3)_2$ (X = H, F, Cl, Br, and OH). The Hartree−Fock data are from Rozhenko et al.,[43] and the other data are from

TABLE 6: CCSD(T)/6-311++G Geometric Parameters for $XP{=}CH_2$ (X = H, F, Cl, and Br) and Partial Microwave Values[a]**

	bond lengths (Å)				bond angles (°)		
	P=C	C−H[1]	C−H[2]	P−X	XPC	H[1]CP	H[2]CP
H	1.684	1.089	1.090	1.422	96.8	124.7	119.4
	1.673	1.09	1.09	1.420	97.4	124.4	118.4
	1.671	1.082	1.082	1.425	97.5	124.5	119.1
F	1.661	1.089	1.090	1.638	102.2	124.5	117.8
	1.646			1.599	104.2		
Cl	1.668	1.088	1.091	2.091	102.1	125.6	117.0
	1.658	1.090	1.078	2.059	103.0	124.6	117.2
Br	1.670	1.088	1.091	2.264	102.2	126.0	116.9
	1.65			2.22	104.0		

[a] Microwave data: references 2 (CH_2PBr); 8 and 9 (CH_2PH); 44 (CH_2PF); 45 and 46 (CH_2PCl). H^1 and H^2 are trans and cis to X, respectively. For each substituent, the CCSD(T) data are in the first row. The second and third rows of data for CH_2PH are from refs 8 and 9, respectively.

this work. The CCSD(T) results should be good predictions for these systems and should be of use in the interpretation of experimental data thereon. Partial structures of the $XP{=}CH_2$ series have been obtained from microwave studies,[2,8,44−46] and it is likely that the dimethyl derivatives will be subjects of similar studies. Another use of the data is to compare B3LYP results with those from CCSD(T), thereby allowing the assessment of B3LYP for studies of larger phosphaalkenes.

In all cases, the molecules studied were found to have C_s symmetry, the C, P, and X atoms being coplanar. As expected, the HF bond lengths are somewhat smaller than the CCSD and CCSD(T) values, most notably for P=C and P−X. The HF C−C bond lengths are larger than the B3LYP values, whereas the reverse is true for the P=C and P−X bond lengths. Going from CCSD to CCSD(T), all bond lengths increase, as is usually observed. The largest effect is for P=C, ~0.01 Å. Except for X = H, the next largest change is for the P−X bond length, followed by those for the C−C bond lengths. The comparison between CCSD(T) and B3LYP bond lengths is interesting, since the B3LYP P=C and C−C bond lengths are smaller than the CCSD(T) values, but the reverse is true for P−X bond lengths. Since basis set extension is expected to *decrease* the CCSD(T) bond lengths, the B3LYP P−X bond lengths are probably somewhat too high. The variation in bond angles between the different methods is minor and less significant than that in the bond lengths.

The effect of substituents on the P=C bond length correlates with the electronegativity of X. The more electronegative X is, the smaller the P=C bond length is. For X = F or OH, the P=C bond length is almost 0.02 Å smaller than for X = H, whereas the difference is ~0.01 Å for Cl and Br. This reduction of the P=C bond length on halogen substitution has been noted by Schoeller et al.[47] in calculations on CH_2PX (X = H, F, Cl, Br, and I), which they attribute to partial ion-pair character (i.e., $X^-PCH_2^+$). The effect of substituents on bond angles can be *qualitatively* rationalized by the relative sizes of hydrogen and the halogens and repulsion between the methyl group and X. Thus, going from H to Br, there is a monotonic increase in both the XPC and C^1CP angles.

For further comparison and because of their intrinsic interest, we have also obtained CCSD(T) structures of the series $CH_2{=}PX$ (X = H, F, Cl, and Br) with the 6-311++G** basis set. These are shown in Table 6. Comparing with the data on the dimethyl derivatives, one can see lengthening of the C=P and P−X bonds when H atoms are replaced by methyl groups.

TABLE 7: CCSD(T)/6-311G C=P and P−X Harmonic Stretching Frequencies (cm^{-1}) and Infrared Intensities (km mol^{-1}) for $(CH_3)_2C{=}PX$ (X = H, F, Cl, and Br)**

	C=P		P−X	
X	ω	I	ω	I
H	969	0.7	2390	144.7
F	979	0.5	773	172.6
Cl	974	0.7	508	117.4
Br	973	0.8	451	61.4

For X = F, Cl, and Br, the C=P bond length increases by almost 0.02 Å, whereas the P−X bond length increase is about 0.01 Å. Methyl substitution has little effect on the HPC and FPC angles, but somewhat more on the ClPC and BrCP angles (2° and 2.5°, respectively). Table 6 also shows microwave structures obtained from isotopic substitution; that is, r_s structures. Of course, there should not be precise agreement with theoretical r_e structures. At the same time, there is good correspondence between the theoretical and experimental results, and they both show the same trends. The good results observed for CH_2PX suggest the reliability of the CCSD(T) structural data for the dimethyl species.

Vibrational Frequencies. The first report of an infrared detection of a phosphaalkene was for CF_2PH.[48] Subsequently, there have been several other infrared observations of small transient phosphaalkenes,[28,49] including CH_2PH and CH_2PCl. Infrared assignments have depended on assigning the unique P=C stretching mode, as well as PX stretching modes. Obtaining reliable assignments has not been easy. In the original assignment for CF_2PH, bands at 1349.5 and 2326.9 cm^{-1} were assigned to P=C and P−H stretches, respectively. However, the first of these is unlikely to be correct. Similarly, the corresponding original assignment for CH_2PH was later revised.[28] The difficulties can presumably be attributed in part to the fact that the mode in question has a relatively low infrared intensity.

In this work, we have calculated harmonic vibrational frequencies of the series $(CH_3)_2C{=}PX$ (X = H, F, Cl, Br) with a view to providing predictions that would be of use in identifying these species. While attempting to analyze the normal modes, however, we found that assigning a mode to the P=C stretch is problematic. In these dimethyl derivatives, there is really no mode that is *principally* a C=P stretch; there is significant mixing with methyl group motions. In each case, we have identified the mode that has most C=P stretching character. As mentioned above, this mode has low infrared intensity. The P−X stretching modes are much more localized and correspondingly much easier to identify. They also have much larger infrared intensities.

We have also calculated harmonic vibrational frequencies and infrared intensities of the parent phosphaalkenes CH_2PX (X = H, F, Cl, Br). These are of interest in their own right, since prior CCSD(T) frequencies of these species are limited, and not all of these species have been observed by infrared spectroscopy. In addition, they have the simplifying feature that the P=C stretching mode is more easily identified. The changes occurring on methyl substitution are instructive.

Tables 7 and 8 show the CCSD(T)/6-311G** harmonic frequencies and infrared intensities for the C=P and P−X stretching modes of $(CH_3)_2C{=}PX$ and $CH_2{=}PX$ (X = H, F, Cl, Br). Comparing the P=C stretching frequencies in Table 7 with the P=C bond lengths in Table 5, one can see the expected correlation: the bond length decreases on going from H to F, then it gradually increases from F to Cl to Br. As noted above,

TABLE 8: CCSD(T)/6-311G *C*=P and P−X Harmonic Stretching Frequencies (cm^{-1}) and Infrared Intensities (km mol^{-1}) for CH_2=PX (X = H, F, Cl, and Br)**

	C=P		P−X	
X	*ω*	I	*ω*	I
H	980	2.0	2398	133.6
F	1003	3.8	757	88.9
Cl	998	0.8	479	109.7
Br	993	1.3	385	62.7

the infrared intensity for the mode that most closely approximates the C=P stretch is small. One can see the same trend in C=P stretching frequencies in CH_2=PX (Table 8), which again is consistent with the bond length changes as a function of X. The C=P stretching frequencies for CH_2=PX are systematically slightly larger (10−24 cm^{-1}) than for the dimethyl compounds, which is consistent with the trend in bond lengths. The situation for the P−X stretches is less straightforward to understand. Comparing Tables 7 and 8, we observe quite large differences between the P−X frequencies in $(CH_3)_2C$=PX and CH_2PX. One factor that may make comparison difficult is the apparent presence of mixing between P−X stretching and HPC bending modes in some of the CH_2=PX.

Conclusions

1. The equilibrium $XP(H)C(CH_3)=CH_2 \leftrightarrows XP=C(CH_3)_2$ (X = H, F, Cl, Br, OH) was studied with CCSD, CCSD(T), and B3LYP methods. There is good consensus between the different methods for energy differences. Except for X = H, the B3LYP results are between the CCSD and CCSD(T) results, indicating the suitability of B3LYP for this type of study.

2. B3LYP was used to study the equilibrium with X = Ar_F. For X = Ar_F, the product is favored significantly more than for X = H, but not as much as for X = F, Cl, Br, OH.

3. Another angle on substituent effects was obtained by studying the deprotonation energy of $XP(H)C(CH_3)=CH_2$. Again, CCSD, CCSD(T), and B3LYP calculations for X = H, F, Cl, Br, and OH showed the same trends. B3LYP calculations with X = Ar_F gave a *smaller* deprotonation energy than for the other substituents.

4. The results of this study are thus in line with suggestions[24] of two possible roles of Ar_F in aiding the formation of phosphaalkenes $Ar_FP=C(CH_3)_2$.

5. CCSD(T) calculations of structures and vibrational frequencies of $XP=C(CH_3)_2$ (X = H, F, Cl, Br) were obtained, which may aid in the interpretation and analysis of future experimental studies. Comparisons were made with the CH_2=PX series.

Note Added in Proof. A reinvestigation of the rotational spectrum of CH_2PH and large basis set CCSD(T) calculations of its structure have been reported,[50] thus providing an improved estimate of the equilibrium structure of CH_2PH.

Acknowledgment. This work was supported by the National Science Foundation (NSF300423-190200-21000, HRD0318519, and HRD0833178). D.J.W. was a student participant in the 2007 CCMSI Summer Institute, supported by NSF-CREST. The ACES II calculations were run on QuantumCube QS4-2800C and QS8-1800C-064 computers from Parallel Quantum Solutions, LLC. We thank Dr. Ajith Perera (University of Florida) for installing ACES II on our QuantumCubes. Most of the Gaussian 03 calculations were run on facilities provided by the Mississippi Supercomputer Center.

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(30) Basis sets in ACES II were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.0, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multiprogram laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830. Contact David Feller, Karen Schuchardt, or Don Jones for further information.

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JP808638S