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

David J. Watts, <u>Ming-Ju Huang</u>, and John D. Watts

Computational Center for Molecular Structure and Interactions, Department of Chemistry, P. O. Box 17910, Jackson State University, Jackson, MS 39217

For a long time, many types of multiple bonds between non-metal elements in the second row of the periodic table (e.g. C, N, O) and third row elements (e.g. Si, P, S) were not known. A common explanation was that the different sizes of 2p and 3p orbitals led to weak pπ-pπ bonding. In the 1980s a significant number of compounds that feature multiple bonds between second- and third-row elements were prepared. The phosphaalkenes, which contain a carbon-phosphorus double bond, are one class of these unconventional compounds. Initial examples included simple short-lived species (e.g. $CH_2=PH$) which were detected spectroscopically.

Later, longer-lived species were prepared, typically containing bulky substituents to improve kinetic stability. Currently phosphaalkenes are no longer only an academic curiosity. A number of applications are developing, including the use of phosphaalkenes as ligands in transition-metal catalysts and in the synthesis of new inorganic polymers.

In this research we have used computational methods to investigate aspects of the synthesis of some isolable phosphaalkenes by Yam et al. (*Inorg. Chem.* **2004**, 43, 3719-3723). Yam et al. used a base-catalyzed tautomerization of $Ar_FP(H)C(R)=CH_2$ to form $Ar_FP=C(R)CH_3$ ($R = CH_3$ or C_6H_5; $Ar_F = 2,6\text{-}(CF_3)_2C_6H_3$ or $2,4,6\text{-}(CF_3)_3C_6H_2$). The substituent Ar_F was thought to favor the phosphaalkene tautomer sufficiently to enable complete conversion. Also, it was expected to increase the acidity of the H atom attached to P in $Ar_FP(H)C(R)=CH_2$, thus facilitating the base-catalyzed hydrogen shift. Calculations were performed with the Gaussian 03 program. We have investigated: (a) the equilibrium between $XP(H)C(CH_3)=CH_2$ and $XP=C(CH_3)_2$ using different X (i.e. $X = H, F, Cl, Br, OH, Ar_F$); and (b) the effect of different X on the acidity of the H in $XP(H)C(CH_3)=CH_2$. Full geometry optimizations were performed with the B3LYP density-functional method using the 6-311G** and 6-311++G** basis sets. Harmonic vibrational frequencies were calculated to confirm that stationary points were local minima. They were also used to obtain ΔH, ΔS, and ΔG at room temperature. CCSD geometry optimizations were also performed for $X = H, F, Cl, Br, OH$ with the 6-311G** and 6-311++G** basis sets. In all cases, the phosphaalkene tautomer is favored and the stability order is $F > Cl > Br > OH > Ar_F > H$. The acidity order, measured by minus the deprotonation energy of $XP(H)C(CH_3)=CH_2$, is $Ar_F > Br > Cl > F > H > OH$, showing the ability of Ar_F to increase the acidity of the H attached to the P. B3LYP NMR chemical shifts (^1H, ^{13}C, ^{19}F, ^{31}P) were compared with the experimental data on $Ar_FP=C(CH_3)_2$. Overall the theoretical and experimental chemical shifts were found to be consistent.