Inorg. Chem. **2002**, *41*, 1320–1322

Inorganic Chemistry
Note

Effects of First-Row Substituents on Silicon–Phosphorus Triple Bonds

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Received April 23, 2001

The chemistry of compounds with low-coordinated phosphorus atoms participating in phosphorus−silicon multiple bonds has faced an astonishing development since the first stable silaphosphene $R_2Si{=}PR'$ was reported by Bickelhaupt and co-workers in 1984.[1−3] However, all of the known stable silaphosphenes have the same molecular skeleton $>Si{=}P-$, containing three-coordinated silicon and two-coordinated phosphorus atoms. In comparison with this, the subject of molecules containing phosphorus−silicon double bonds (i.e., $Si{=}P-$, possessing one-coordinated silicon and two-coordinated phosphorus atoms) is rather poorly explored. Also, to the best of our knowledge, there have been no reports of the characterization of compounds with a $Si{\equiv}P$ triple bond. A possible explanation for the nonexistence of such multiply bonded compounds is the electronegativity difference ($x(P) - x(Si) = 0.3$).[4] This may result in the silicon−phosphorus π-system being rather polarized, readily leading to dimerization or polymerization.

In this work, we examine theoretically the existence and relative stabilities of such $-Si{\equiv}P$ triply bonded molecules, in which the silicon and phosphorus have coordination numbers 2 and 1, respectively, in comparison with other possible double-bonded isomers (especially those containing the $Si{=}P-$ skeleton). Therefore, we have studied phosphasilynes $XSi{\equiv}P$ with various substituents (X) on silicon to determine the factors which influence the stabilization and some molecular properties. In view of the situation, theoretical information is of great help in further advancing phosphasilyne chemistry. Thus, we have undertaken the first theoretical calculations of the properties of the series of phosphasilyne ($XSi{\equiv}P$; X = H, Li, BeH, BH_2, CH_3, NH_2, OH, and F) molecules to extend the knowledge of silicon−phosphorus triple bonds.[3] To investigate their stabilities, comparisons with $XSi{\equiv}P$ and $Si{=}PX$ (phosphasilene) are made using results obtained at the same level of theory.

With a proper choice of substituents, silicon−phosphorus triple bonds are found to be thermodynamically and kinetically more stable than silicon−phosphorus double bonds. Successful schemes for the synthesis and isolation of phosphasilynes are expected to be devised soon.

Three regions on the potential energy surfaces are considered in this work: $XSi{\equiv}P$ (phosphasilyne), the transition states, and $Si{=}PX$ (phosphasilene). Their geometries and energetics have been calculated using nonlocalized DFT in conjunction with the 6-311++G(d,p) basis set, which is denoted as B3LYP/6-311++G(d,p) (hereafter designated B3LYP).[5] All the stationary points have been positively identified as equilibrium structures (the numbers of imaginary frequency (NIMAG = 0)) or transition states (NIMAG = 1). Single-point energies were also calculated at CCSD(T)-(frozen)/6-311++G(3df,3pd)//B3LYP/6-311++G(d,p) (hereafter designated CCSD(T)) to improve the treatment of electron correlation. Unless otherwise noted, relative energies given in the text are those determined at CCSD(T) and include vibrational zero-point energy (ΔZPE) corrections determined at B3LYP/6-311++G(d,p).[6]

The calculated potential energy surfaces for the reaction (1) $XSi{\equiv}P \rightarrow TS \rightarrow Si{=}PX$ (X = H, Li, BeH, BH_2, CH_3,

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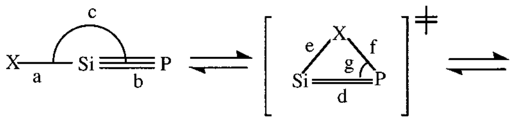
10.1021/ic0104252 CCC: $22.00

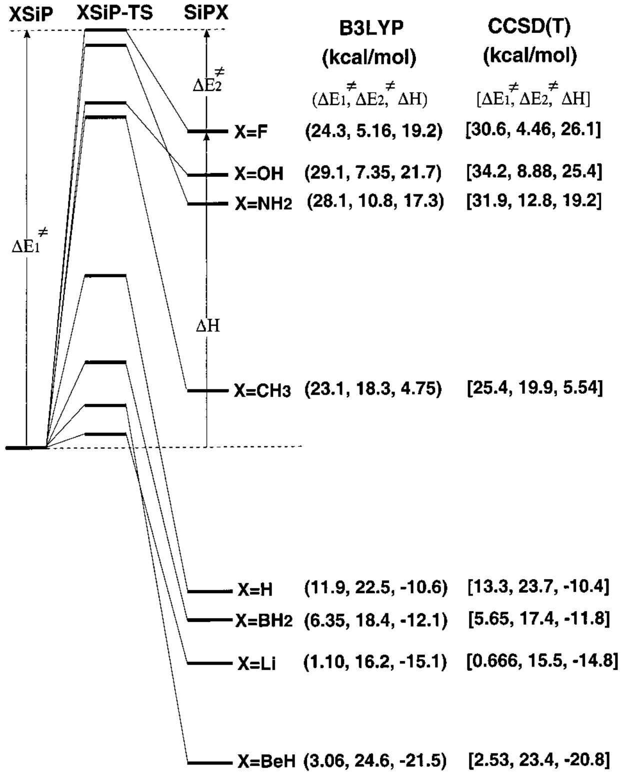
Table 1. Geometrical Parameters of the Structures for Eq 1 at the B3LYP/6-311++G(d,p) Level of Theory (Distances (Å), Angles (deg))



(1)

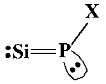
X	a	b	c	d	e	f	g	h	i	j
H	1.480	1.957	180.0	2.045	1.524	2.491	37.68	2.063	1.490	61.89
Li	2.406	1.987	180.0	1.996	2.393	3.976	27.58	2.032	2.304	79.68
BeH	2.142	1.975	180.0	1.997	2.130	3.492	33.40	2.055	2.004	84.35
BH_2	1.971	1.977	180.0	2.021	2.027	2.608	50.00	2.055	1.885	111.1
CH_3	1.878	1.959	180.0	2.058	2.023	2.827	45.63	2.079	1.941	77.77
NH_2	1.696	1.962	180.0	2.145	1.792	2.766	40.38	2.093	1.712	121.7
OH	1.636	1.959	178.8	2.181	1.727	2.735	39.13	2.124	1.694	108.4
F	1.606	1.956	180.0	2.200	1.698	2.649	39.64	2.125	1.948	55.96

Scheme 1

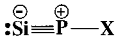


NH_2, OH, and F) are presented in Scheme 1. Also, the relative energies of $XSi{\equiv}P$, $Si{=}PX$, and the transition state (TS) connecting them at the B3LYP and CCSD(T) levels of theory are included in Scheme 1 for comparison. Selected geometrical parameters predicted at DFT for these stationary points are given in Table 1. The calculated vibrational frequencies, rotational constants, dipole moments, and net atomic charges of XSiP and its derivatives are collected in Table 2 in the Supporting Information.

As one can see in Table 1, all the triple bond species ($XSi{\equiv}P$) preferentially take up a linear structure, whereas for the double bond isomers ($Si{=}PX$) a bent rather than linear structure is observed. The reason for the latter case may be due to the phenomenon of orbital nonhybridization. That is to say, the phosphorus atom is reluctant to take part in hybridization (eq 1, *f*). Thus, it tends to form a nonbonding orbital acquiring mainly s-character, while the remaining p-electrons are used up to form bonds with the neighboring atom. As a result, the formation of an sp-hybrid orbital is disfavored and bent $Si{=}PX$ (**1a**) becomes considerably more stable than its linear structure (**1b**). Consequently, from our DFT calculations on the model compound $Si{=}PX$, it is concluded that bent structure **1a** is the best representation of its conformation.



1a



1b

As shown in Scheme 1, the order of stability of $XSi{\equiv}P$ and $Si{=}PX$ is highly dependent on the substituent X. On one hand, electropositive-substituted $XSi{\equiv}P$ molecules lie above the corresponding $Si{=}PX$ isomer by 10 (X = H), 15 (X = Li), 21 (X = BeH), and 12 (X = BH_2) kcal/mol at the CCSD(T) level of theory. On the other hand, substitution of an electronegative group at silicon can dramatically lower the energy of the $XSi{\equiv}P$ molecule with respect to that of the corresponding $Si{=}PX$ species. For example, the CCSD(T) results suggest that $XSi{\equiv}P$ is now more stable than $Si{=}PX$ by 26 (X = F), 25 (X = OH), 19 (X = NH_2), and 5.5 (X = CH_3) kcal/mol. The relative stability of triply bonded and doubly bonded species has therefore been reversed.

Besides this, as Scheme 1 shows, electronegative substitution not only stabilizes the formal triple bond structure relative to the phosphasilene isomer, but also results in a larger forward activation barrier ($\Delta E_1^{\ddagger}$, left to right in eq 1) as well as a smaller reverse barrier height ($\Delta E_2^{\ddagger}$, right to left in reaction 1). For instance, the CCSD(T) calculations suggest an increasing trend in $\Delta E_1^{\ddagger}$ (in kcal/mol) for X = OH (34) > X = NH_2 (32) > X = F (31) > X = CH_3 (25), which are apparently larger than those for X = H (13) > X = BH_2 (5.7) > X = BeH (2.5) > X = Li (0.67). These results mirror the trend in $\Delta E_2^{\ddagger}$ (kcal/mol) for the reverse process: X = F (4.5) < X = OH (8.9) < X = NH_2 (13) < X = CH_3 (20), which are obviously smaller than those for X = H (24) > X = BeH (23) > X = BH_2 (17) > X = Li (16). As a result, this investigation provides strong evidence that the $XSi{\equiv}P$ triply bonded molecule with electronegative substitution at silicon is both kinetically and thermodynamically more stable than the corresponding $Si{=}PX$ doubly bonded isomers.

The large energy difference favoring $XSi{\equiv}P$ over $Si{=}PX$ may be due to two factors. In the first place, according to some experimental work,[7] some available bonding energies (kcal/mol) of the Si−X and P−X bonds are as follows: Si−F (132), P−F (105 ± 23); Si−O (191 ± 3.2), P−O (143 ± 3.0); Si−N (112 ± 3.6), P−N (147 ± 5.0); Si−H (≤71.5), P−H (71.0); Si−C (108), P−C (123); Si−B (68.9), P−B (82.9 ± 4.0). As a consequence, it is evident that a strong Si−X bond and a weak P−X bond can greatly stabilize the $XSi{\equiv}P$ triple-bonded structure with respect to the $Si{=}PX$ double-bonded isomer. Second, as one can see in Table 1, it appears that electronegative substitution (such as X = F, OH, NH_2, and CH_3) strengthens the $Si{\equiv}P$ triple bond, whereas electropositive substitution (e.g., X = H, Li, BeH, and BH_2) weakens this triple bond. This effect on the $Si{\equiv}P$ bond distance in the phosphasilyne can be explained in terms of bond polarity. It is well-known that the silicon−phosphorus bond is polarized due to the electronegativity difference between the two atoms. Hence, the $Si{\equiv}P$ bond is expected to be highly polarized with silicon as the positive pole, while the P atom carries a negative charge (i.e., $Si^{\delta+}{\equiv}P^{\delta-}$). When an electron-withdrawing substituent is attached to the silicon atom, this induces a large positive charge on the attached Si atom and a small increase in electron density on the germinal P atom. However, electropositive substitution has the reverse effect. As a result, the more electronegative the substituent X attached to silicon, the more positive the charge at silicon, the higher the degree of bond ionicity, and the shorter the $Si{\equiv}P$ triple bond. Conventionally, it is agreed that the shorter the bond distance, the stronger the bond strength. Accordingly, from the above discussion, it is clear that both of these considerations can overturn the large intrinsic preference of $Si{=}PX$ over $XSi{\equiv}P$.

Finally, considering the steric effect, our model calculations indicate that methyl substitution for reaction 1 is predicted to be nearly degenerate in energy, $H_3CSi{\equiv}P$ being slightly more stable than $Si{=}PCH_3$ by 5.5 kcal/mol at the CCSD(T) level. Additionally, the activation barrier ($\Delta E_1^{\ddagger}$) for 1,2-CH_3 shift of $H_3CSi{\equiv}P$ is estimated to be 25 kcal/mol, while the barrier height ($\Delta E_2^{\ddagger}$) for the reverse process is predicted to be 20 kcal/mol. Consequently, if $H_3CSi{\equiv}P$ and/or $Si{=}PCH_3$ were directly formed by the appropriate experiments, they should not easily interconvert. In other words, our theoretical findings suggest that the steric protection of the linear grouping of atoms in the $XSi{\equiv}P$ triply bonded system should be possible as it is in the case of the $Si{=}PX$ doubly bonded system.

In summary, our theoretical investigation supports the idea that electronic and steric effects play a significant role in determining the relative stability of phosphasilyne and phosphasilene. Although silicon and phosphorus are two elements that are notoriously reluctant to form p−π multiple bonds,[1,2] electronegative substitution on silicon preferentially stabilizes the formal triple bond ($XSi{\equiv}P$) relative to the double bond ($Si{=}PX$). In particular, fluorine-substituted phosphasilyne (i.e., $FSi{\equiv}P$) is the most promising candidate for isolation as a long-lived molecule.

We encourage experimentalists to design further experiments to confirm our predictions.

Acknowledgment. We are grateful to the National Center for High-Performance Computing of Taiwan for generous amounts of computing time. We thank the National Science Council of Taiwan for its financial support. We also thank the reviewers for their helpful suggestions in improving the manuscript.

Supporting Information Available: Table 2 giving the calculated harmonic vibrational frequencies, rotational constants, dipole moments, and net atomic charges of the stationary points in XSiP isomerization reactions at the B3LYP/6-311++G(d,p) level of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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